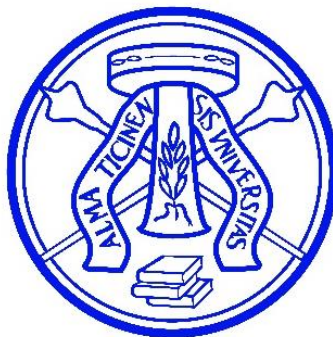




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**DOTTORATO IN SCIENZE CHIMICHE E FARMACEUTICHE E
INNOVAZIONE INDUSTRIALE
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Tesi di Dottorato di
Giulia Giovilli

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Tutor

Chiar.ma Prof.ssa Chiara Milanese

Co-tutor

Chiar.mo Prof Lorenzo Malavasi

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Table of Acronyms

Acronym/Abbreviation	Definition
4-ATP	4-aminothiphenol
A/D	Acceptor/Donor
a-BMO	amorphous Bi_2MoO_6
a-BWO	amorphous Bi_2WO_6
AQY	Apparent Quantum Yield
BMO	Bi_2MoO_6
BWO	Bi_2WO_6
CAES	Compressed Air Energy Storage
CB	Conduction Band
CBM	Conduction band minimum
c-BMO	crystalline Bi_2MoO_6
c-BWO	crystalline Bi_2WO_6
CTAB	Cetrimonium bromide
DCD	Dicyandiamide
DDT	Deflagration-to-Detonation Transition
DFT	Density Functional Theory
DI	Distilled
FC	Fuel Cell
g-CN	graphitic carbon nitride, g- C_3N_4
GC-TCD	Gas Chromatography - Thermal Conductivity Detection
GHG	Greenhouse Gas
H-B	Haber-Bosch
HER	Hydrogen Evolution Reaction

HTEL	High Temperature co-Electrolysis
ISE	Ion selective electrode
LOHC	Liquid Organic Hydrogen Carrier
MADLS	Multi-angle dynamic light scattering
MOF	Metal-Organic Framework
MSR	Methane-Steam Reforming
NHE	Normal hydrogen electrode
NIR	Near Infrared
NP	Nanoparticle
NR	Nanorod
NRR	Nitrogen Reduction Reaction
NS	Nanosphere
NSs	Nanosheets
OER	Oxygen Evolution Reaction
OP	Oxidation Photocatalyst
PANI	Polyaniline
PCET	Proton-Coupled Electron Transfer
PCN	Porous g-C ₃ N ₄
PEM	Proton-Exchange Membrane
PHE	Photocatalytic Hydrogen Evolution
PIA	Photoinduced absorption
PNF	Photocatalytic Nitrogen FIxation
PS	Photocatalyst
RE	Renewable Energy
RP	Reduction Photocatalyst
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscope

SI	Supporting Informations
S-M	Semiconductor-Metal
SOEC	Solid-Oxides Electrolysis Cell
SPR	Surface Plasmon Resonance
S-S	Semiconductor-Semiconductor
STH	Solar-To-Hydrogen
TEAO	Triethanolamine
TST	Tri-s-triazine
UV	Ultraviolet
VB	Valence Band
VBM	Valence band maximum
VdW	Van der Waals
Vis	Visible
VLA	Visible-Light-Active
VLD	Visible-light-driven
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Chapter 1

1. Introduction

1.1 Energy: a hot commodity

One of the most challenging concern of the 21st century is the increasing energy demand due to the ever-expanding world population – expected to reach between 9 and 10 billion by 2050 – mostly in developing nations.: their access to the energy supply chain is still not guaranteed and their development further delayed.^[1,2] Because fossil resources (natural gas, coal and oil) are still the most predominant energy source in global production, their use is a key-factor in the increasing concern over greenhouse gas (GHG) emissions, energy security and availability, and climate change.^[3,4] At the current consumption rates, coal's availability as a fuel is estimated to be 150 years while gas and oil supplies only 52 years, and there will be no more uranium in a few decades. The rapid globalization rate has considerably decreased the estimated lifetimes of non-renewable resources, while the estimated increase in the global energy demand will be 28% by 2040.^[2]

Anthropogenic climate change is a consequence of more than a century of net GHG emissions (with CO₂ being the most impactful) from energy use (electric production is responsible for the largest amount of CO₂ emissions, 28%), land-use and land-use change, lifestyle and patterns of consumption, and production (e.g. cement manufacturing and ammonia production). CO₂ is a very important component of Earth's atmosphere because it absorbs infrared radiation, responsible for much of the greenhouse effect that keeps the planet warm, and also – when its concentration rises significantly – for global warming and climate change.^[1] Globally, 2024 was the warmest year on record and the first in which the average temperature exceeded 1.5°C above the pre-industrial level: the intensification of climate change brought a surge of extreme weather events with severe and

widespread impacts, while glaciers across Europe continue to melt – with those in the Alps among the fastest shrinking in the world^[5].

The extraction of fossil fuels – conventionally easy in the case of coal and natural gas, and increasingly harder for oil - and their refinement is still causing irreversible environmental damages like deforestation, water pollution and habitat destruction. The decreasing oil reserves are also one of the most important geopolitical battle ground^[6]: hence, breaking from the chokehold fossil fuels have on global economies is imperative for the betterment of the human condition.^[7]

The European Green Deal (2019) aims to cut emissions by at least 50% by 2030 and legally binds the European climate-neutrality goal of net zero GHG emissions by 2050 through the European Climate Law.^[8] In 2024, the total net GHG emissions decreased by 2.5% compared to 2023, 32.7% lower than in 1990, continuing with its downward path. The energy sector achieved the most significant decrease (8.6%, or 66 metric tons of CO₂ equivalent) compared to 2023: the power sector factored hugely in this decrease, thanks to an 8% increase in electricity generated from renewables and a 5% rise in nuclear power, coupled with a decrease in gas by 8% and coal by 12%.^[5]

Renewable energy (RE) sources are thus continuously identified as a fundamental component of the green transition toward a low carbon future: at present energy sources other than fossil fuels – renewable resources like wind, solar and geothermal, but also nuclear fission, hydroelectricity and biomass - make up less than 20% of global energy consumption.^[1]

1.2 Renewable energy: a step toward the future

Other than using sustainable energy sources like sunlight, wind, tides and biomass, RE resources can potentially open the access of a broader geographical area, most of all in developing and underdeveloped countries, to the energy supply chain. RE technologies convert energy harvested from sustainable sources into electrical, chemical and/or mechanical energy: all are used to produce electricity, but so far only geothermal, solar and biomass have been used for heat generation.^[2]

The major advantages of RE resources are the non-finite supply, less maintenance than conventional generators, decreased operating costs due to the naturally derived fuel, lower environmental impact due to the very little – in some cases even zero – emitted quantity of CO₂ and other chemicals pollutants. There are also some disadvantages associated with the usage of RE resources: one is the lowered capacity of RE-based electricity and the other is supply instability, most of all for REs that rely on compatible weather conditions (like solar and wind).^[9]

When comparing solar power conversion and wind energy to fossil fuels, power generation is highly intermittent: during peak operation, RE sources are able to surpass the requested energy quantities during production. When energy storage technology is integrated in the energy grid, there's a way to manage this intermittency, thus increasing the efficiency of the power supply and enabling surplus energy to be stored during periods of high production and retrieved during periods of high demand or low generation.

Some of the technologies considered for this includes pumped hydro, compressed air energy storage (CAES), lithium-ion batteries, and hydrogen^[3]: among these, batteries (or electrochemical accumulators) are the most widely adopted due to their high round-trip efficiency and rapid response abilities, but their use still comes with major limitations, like energy density, weight, and scalability, making them ill-suited for large-scale deployment. The long term-sustainability of critical raw materials such as lithium and cobalt^[10], typically present in batteries, raises up concerns regarding resource depletion and environmental impact.^[11] Alternative energy storage solutions to batteries have been popping up and gaining traction, and hydrogen stands out as one of the most promising ones: storing energy in molecular bonds, like the ones in hydrogen molecules, doesn't suffer from self-discharge, meaning that long storage times aren't accompanied by energy loss.^[12]

1.3 Hydrogen: a renewable fuel

Discovered in 1776 by Henry Cavendish, hydrogen (greek for *water-generator*) is the most abundant element of the universe and the third most abundant on Earth. When we talk about hydrogen,

we talk about its molecular form, H_2 , a colorless, odorless and tasteless gas. In nature, hydrogen is found usually in heterogenous molecules, like water or hydrocarbons. The hydrogen gas, very useful for energetic purposes, doesn't exist naturally and can't be extracted like other fuels: it must be produced.

Hydrogen has a very long-term viability – its estimated availability is virtually the same length of time as the existence of the human race: its production is not geographically-bound and there are various methods to execute it, some more and some less environmentally conscious.^[13–15] It can be used by a wide range of consumers, going from a micro-scale to a mega-scale: turbines, internal combustion engines and fuel cells, as well as oven and heaters. Thanks to the absence of moving parts in some of these systems, their efficiency and life span are higher than conventional ones. Harmful emissions due to its consumption are minimal, because water is the only byproduct.^[6,16] Hydrogen can be added to other fuels to create energy-enriched mixtures, but also used directly as an alternative fuel for engines not explicitly designed for hydrogen-use.^[17,18] Differently from conventional fossil fuels, it has a very small and light molecular structure.^[19]

Hydrogen natural state at ambient temperature is that of a gas - fuel needs to be in either a gaseous or vaporized state to be burnt - and its flashpoint (in the presence of an ignition source and exposed to air, it's the temperature at which a type of fuel generates enough heat to form a flame on its surface) is $-231^{\circ}C$, lower than most common fuels^[20]: the expected starting and ignition equipment needed for a hydrogen-fueled engine are thus simpler and could work in “harsher” condition, like after being left unignited in the cold for days. The flammability range (the fuel-air ratios that are still ignitable) is between 4-75% and its much higher than some comparable fuels, meaning that no enhancements or additional systems like turbochargers need to be included to perform better in low pressure situations.^[21] This means that switching to hydrogen as a primary fuel doesn't imply an entire overhaul of the infrastructures already in use.

Hydrogen is especially attractive for large-scale grid storage because of its: high gravimetric energy content (143 MJ kg^{-1} , 2.5-3 times higher than the most commonly used fossil fuels), zero CO_2 emissions and possible employment as back-up power generation in conjunction with fuel cells (FCs). Unlike traditional combustion engines, fuel cells generate electricity through an electrochemical reaction between hydrogen and oxygen, with heat and water as by-product and no need for carbon-based fuels; they are silent, highly efficient (70-80% conversion), and produce zero emission at the point of use. They are already in action in several sector, including transportation, stationary power generation, and portable devices: versatile and efficient, their application is a huge boon for carrying forward a sustainable energy transition. Thus, within a vehicle or an industrial power generation facility, for every kilogram of stored hydrogen burnt, the energy generated is about 2.5 to 3 times higher than conventional fossil fuel. But in its natural state, hydrogen is a gas with very low density (in ambient conditions, $d_{\text{H}_2 \text{ gas}} = 0.084 \text{ g} \cdot \text{L}^{-1}$ and $d_{\text{H}_2 \text{ liquid}} = 70,8 \text{ g} \cdot \text{L}^{-1}$), definitely lower than most fossil fuels, and as such its volumetric energy density is lower than what's achievable with fossil fuels: any media storing hydrogen will have to deal with either volumetric penalties (the energy per unit volume released by hydrogen is 1/2650 of gasoline) or, if liquefied to decrease the storage space necessary, a heightened energy consumption to store it under pressure.^[6] So, storing and transporting hydrogen under pressure requires additional energy; also, converting that stored hydrogen into electricity through the use of a fuel cell comes at a cost (a loss of 20-30% of the hydrogen fuel).

Hydrogen as energy storage entails a significant loss - about 50% of the initial electrical energy - that can, however, be curtailed by local or within-short-distance production and use, like in the case of small home reactors. Transportation for public and commercial use, that moves through a fixed route (like buses, but also ships, heavy vehicles and airplanes), is also an ideal candidate because it requires less production and refueling stations.

Today, the major drawbacks of increasing hydrogen use are overall lifecycle costs (production and supply cost, market price, demand, storage, distribution and investment costs) and perception over fuel safety.

Considering the safety aspects, hydrogen is not toxic, but extremely flammable thanks to: its laminar burning, its buoyant and propagation velocities being significantly higher than those of common fuels, and its flame temperature in the presence of ambient oxygen content being almost the same as common fuels.^[6,15,16] However, its vapor-from-liquid generation speed is much higher and, because of that, hydrogen fires lasts a 10-20% of the time of a same-volume fossil-fuel fire, but smoke inhalation isn't harmful because it's just water vapor. A big safety hazard of hydrogen fires is that flames are nearly invisible in daylight, making fire detection harder and slower.^[6]

Hydrogen's biggest advantage is also its biggest handling drawback, sensitivity to detonation: turbulent flame speeds easily exceed 800 m s^{-1} and can reach several km s^{-1} thanks to high laminar burning velocity and flame speed. It also has a wide flammability range, making it more sensitive to the deflagration-to-detonation transition (DDT) than hydrocarbons.^[16] On the other hand, its auto-ignition temperature, 585°C , is the highest when compared to other more common fuels and, differently from them, it's also unaltered by increasing pressure and oxygen concentration.^[22] However, that's coupled with the very low electro-conductivity rating of hydrogen; both liquid- and gas-state flow and agitation can be a concern for its handling, because the formation of electrostatics charges is able to trigger sparks. Therefore, all equipment in direct contact with hydrogen should be electrically grounded.

In regards of all stated safety concerns, hydrogen has been safely produced, stored and transported for several decades already, and its storage and use doesn't really present any significant additional risks than other fuels, be they liquid or gas^[16].

Production is what majorly drives up the hydrogen cost, because the primary source from which hydrogen is extracted are still fossil fuels (in 2008, only 4% of the hydrogen produced was obtained without the use of fossil fuels), exacerbating the carbon cycle. Not only this extraction comes with a considerable energy loss, but also with high costs needed to implement extraction systems; adding this additional step in the energy production cycle means producing a fuel that is much costlier and with lower energy-content for the end-use application, if we consider well-to-wheel efficiencies.^[3] Hydrogen obtained via renewable energy powered electrolysis allows for better well-to-wheel efficiencies and a potentially cheaper fuel overall.

1.4 Hydrogen production: an industrial perspective

Several processes can be used in the production of hydrogen - thermochemical, electrochemical, photochemical, photoelectrochemical and photocatalytic – but the sources of hydrogen are only three: fossil fuels, biomass and water.

1.4.1 Fossil fuels

Fossil fuels, usually made of large and heavy hydrocarbon structures, are the most common sources from which hydrogen is extracted: they include coal^[23], gasoline, oil (heavy and light), methanol, methane^[16] and biomass^[24].

The methods used for hydrogen “extraction” from hydrocarbons focus on cleaving bonds between hydrogen and carbon atoms. The most common – almost 48% of the global hydrogen produced – and economical method of hydrogen production is methane-steam reforming (MSR), a highly endothermic process in which methane reacts with steam to produce a mixture of H₂, CO₂ (producing nearly 10 kg of CO₂ for every kg of H₂) and CO at temperatures in the range of 700 and 1000°C, pressures between 3 and 25 bar and in the presence of a metal catalyst composed mainly of nickel^[25]. Almost all of the hydrogen produced through MSR, called *grey hydrogen* or *blue hydrogen* depending on the absence or the presence of carbon-capturing technologies^[26], a by-product of oil

refinement, because reformation is a process used to increase the octane level within a hydrocarbon mixture.^[27] The efficiency of MSR is 65-75% in the best case for commercial productions, and any efforts to increase the efficiency would have a significant impact on the hydrogen economy.

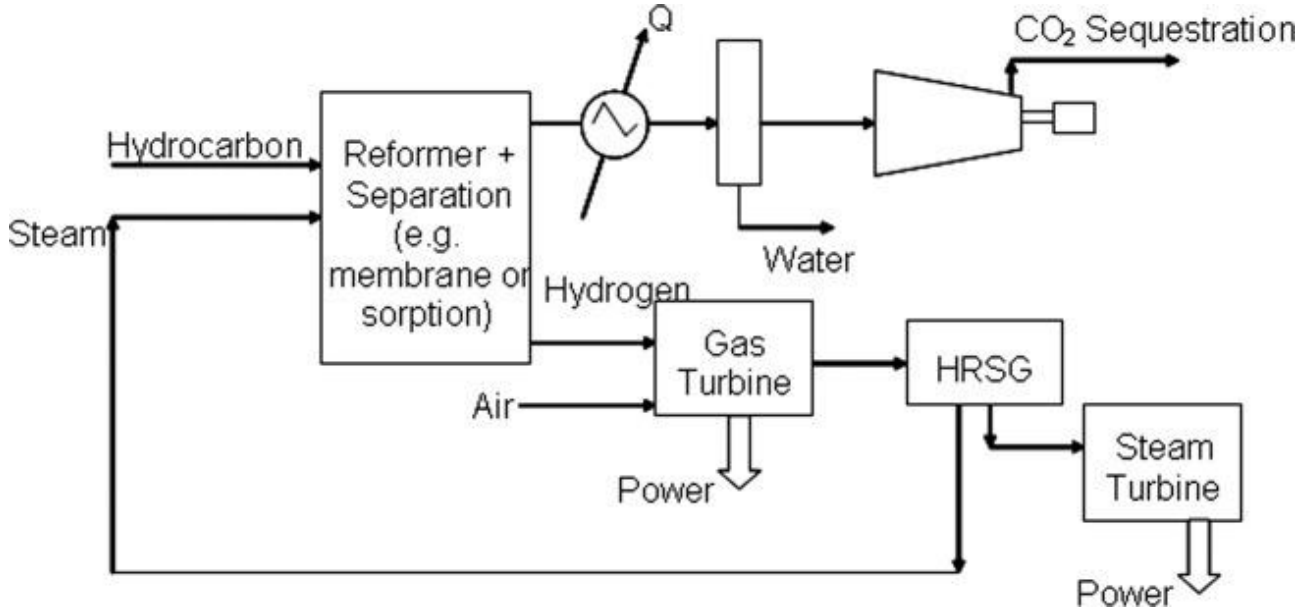


Figure 1. Steam-Methane Reforming and post-processes. Copyright 2009, Wiley²⁷

Coal and oil follow in the second and third place, with 30% and 18% of hydrogen produced globally.^[15] The advantages of using fossil fuels start and end with a large scale production that is reasonably priced, while still emitting CO and CO₂ and using finite resources, making it incompatible with a sustainable transition to a global decarbonized economy.^[28]

1.4.2 Biomass

Biomass has attracted a lot of attention for hydrogen production because it couples an approach that has a lower environmental impact than fossil fuels (CO₂ emissions are lower, but not zero) with a feedstock considered renewable and sustainable, because it's produced naturally from biological sources.^[4] Biomass is readily available in many forms, such as agricultural waste, waste from forests, municipal waste, industrial waste, aquatic biomass, and terrestrial biomass, but also food processing waste, wood-related municipal solid wastes, and oil seed crops. The most important process used to produce green hydrogen from biomass is biomass gasification; compared to the

syngas obtained from biomass combustion or pyrolysis, this syngas is cleaner, higher in energy and also more advantageous in terms of the specific heat capacity.^[29,30]

The gasification reaction mechanism starts with the drying (removal of moisture) of the biomass feedstock at a gasification reaction temperature of 110 °C. Then, the dried biomass is pyrolysed to obtain biomass pyrolytic solid and pure carbon (char) at a temperature lower than 500 °C. The third and fourth steps are the partial oxidation and reduction of the biomass pyrolytic solid, respectively, in which all the main gasification reactions involving a gasifying agent (air/O₂/CO₂/steam) take place. Using steam as the gasifying agent enhances the water-gas shift reaction, resulting in higher amount of H₂ and CO generated.^[29]

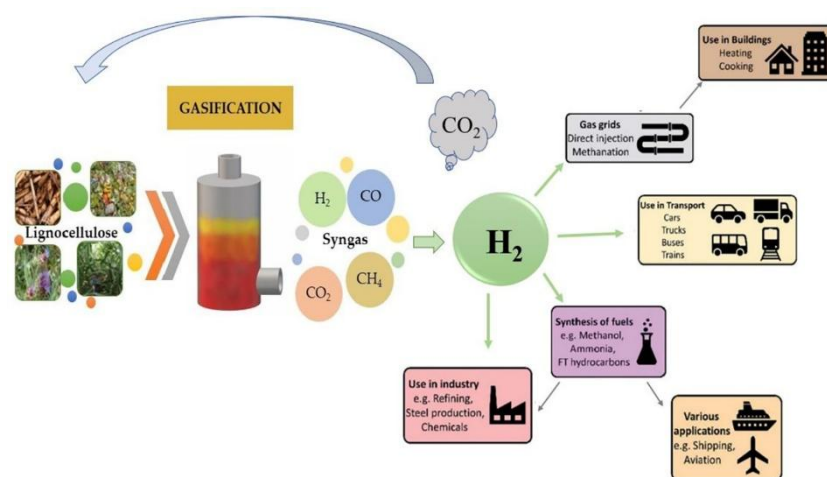


Figure 2. Biomass gasification. Copyright 2023, Elsevier³⁰

Biomass gasification is an emerging technology and, in the present form, there are few obstacles to its application, in terms of technical and economic barriers: the technical challenges (unreliability of the gasifying equipment, lack of secondary pollution handling and the inability to finetune the product obtained) stem from the newness of the gasifying technology, while the economic barriers include exorbitant transportation costs of biomass, lack of investment channels, and high electricity price.^[29]

1.4.3 Water

Hydrogen produced by water electrolysis, called green hydrogen^[26], is a clean and sustainable energy carrier with the smallest share of the market, 4% (approximately 65 million metric tons), among the large-scale methods. This technology is one of the oldest known electrochemical process: water electrolysis has been known since the late 19th century, but its industrial application didn't gain traction until the early 20th century, when more than 400 alkaline electrolyzers were in operation.^[4]

Interest in water-splitting as a mean of hydrogen production has been increasing in recent years, thanks to the steady reduction of RE costs; it is the most studied approach for producing green hydrogen on a wide-scale.^[31] Additionally, hydrogen can be converted into ammonia or synthetic hydrocarbons to more easily exploit existing infrastructure and to be used as fuel or raw material in various industries.^[32]

Electrolysis is a chemical process in which electricity drives a non-spontaneous reaction: in water-splitting, water molecules, either in the liquid phase or as steam, are subjected to an electric current and split into their elemental components. The device used in this process is called electrolyzer, where electric currents pass through water with the help of electrodes separated by an ionic conducting medium. The half-reactions happening at the electrodes are:



The biggest challenges to raising the scale of this process are the high production costs, due to high capital investments, low conversion efficiency, and electrical power cost. Because of this, water-splitting is still far from being the method of choice for industrial scale production and electrolytic hydrogen is still unable to really compete with traditional fuels.^[33] At full conversion efficiency, the electrolytical process requires a minimum of 39.4 kWh kg⁻¹; however, typical electrolyzers consume up to 50 kWh to produce just 1 kg of hydrogen. Thanks to progressing energy technologies, high electrical expenses can be offset by the use of renewable energy, whose cost has

been going down year by year: e.g. the price for solar photovoltaic modules is 1% of what it was in 1980s, and it expected to decrease more going forward.^[34] Electrolyzers can be easily located close to renewable energy sources, reducing the length of distance transmission lines and minimizing energy loss. Considering the significant amount of energy wasted during off-peak times at several renewable energy power plants with no energy storage, using this energy for water electrolysis can further reduce power costs. Hydrogen's not a primary energy source, but an energy carrier because it's not found as is in nature; thus it's capable of storing the energy obtained through renewable energy sources.^[3]

The oldest technology employed for electrolytic hydrogen production is alkaline water electrolysis: this type of electrolyzer uses a liquid electrolyte, usually potassium hydroxide (KOH) or sodium hydroxide (NaOH), and works between 60 and 80°C, relatively low temperatures. When a current is provided, hydroxide anions (OH⁻) move from the cathode to the anode while the electrodes are submerged in the electrolyte; this results in the formation of oxygen at the anode and hydrogen at the cathode. A diaphragm between the electrodes prevents the mixing of oxygen and hydrogen, avoiding the formation of explosive mixtures. Alkaline water electrolysis is a fully settled technological process with achievable conversion efficiencies between 70-80%: advantages are low investment costs, longevity and minimal reliance on critical raw materials. But, because of slow electrolyte circulation, this technology is also characterized by a challenged dynamic load responsiveness.^[35,36]

Alkaline water-electrolysis also present additional issues when paired with fluctuating power sources - like when integrated within a RE grid – for example a decrease in gas purity and under partial loads and degradation issues. Other significant barriers are the high investment costs needed to set up the system, efficiency declining in colder temperatures (making it less effective in colder regions and seasons), removal of impurities from the water source to avoid a reduction of the process

effectiveness, operational costs increased by regular maintenance. Moreover, the slow hydrogen generation can potentially delay hydrogen-dependent tasks.

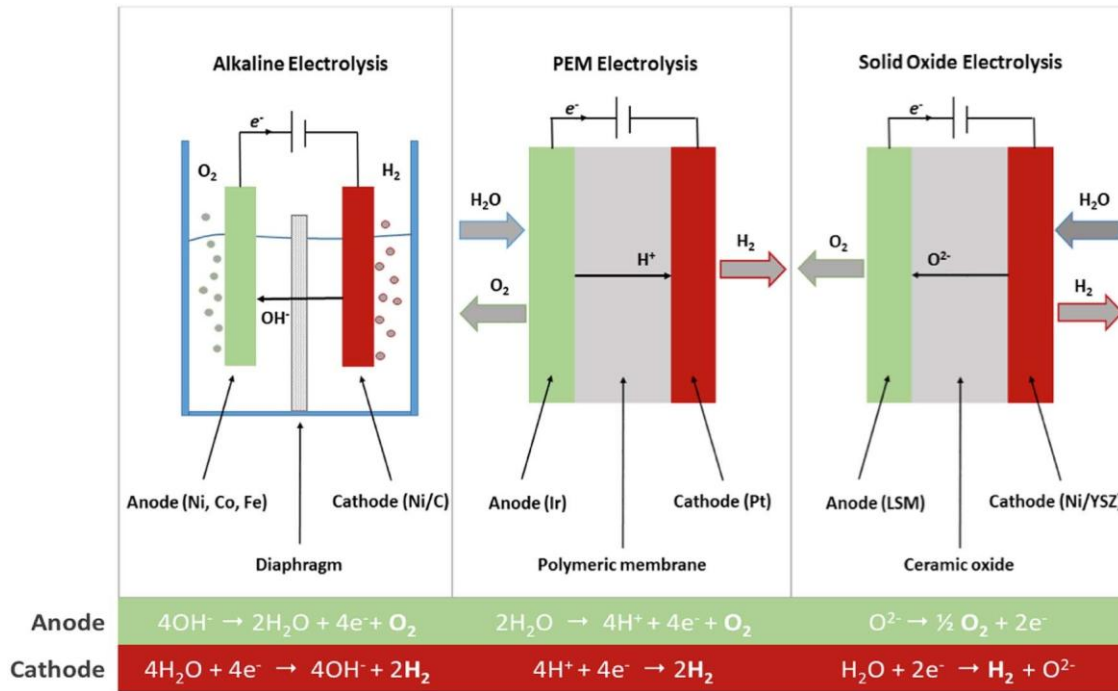


Figure 3. Operation principles of alkaline, PEM (proton-exchange membrane) and solid oxide water electrolysis. The overall reaction is $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$. Oxygen evolution occurs at the anode, hydrogen evolves at the cathode. The case of solid oxide electrolysis shown is that of an O^{2-} -conducting electrolyte, with a nickel/yttria-stabilized zirconia cathode and a lanthanum strontium manganite (LSM) anode. Copyright 2017, Elsevier³⁶

PEM (proton-exchange membrane) electrolysis is widely regarded as one of the most advanced and efficient methods for producing *green* hydrogen from RE sources, including wind, solar photovoltaic, and hydropower. PEM electrolyzers use a solid polymer electrolyte and operate at higher current densities, contributing to a more compact system design and enables rapid response times. ^[4] This technology is capable of producing hydrogen at a greater rate, with an exceptional purity level of 99.99%. Additionally, PEM electrolysis is noted for its high energy efficiency, ranging between 80–90%, and its capability for high dynamic operation. However, it's a relatively new and only partially established technology, that faces obstacles such as the high cost of components. The

acidic operational environment can lead to low durability of the system. Furthermore, while commercialization is on the horizon, it is still considered to be in the near term, indicating that wider market adoption has yet to be fully realized.^[37]

Finally, high-temperature co-electrolysis (HTEL) of CO₂ and steam couples the transformation of CO₂ into CO and the production of hydrogen to form syngas, thanks to the application of solid oxides electrolysis cells (SOEC), that works at temperatures from 500 to 900°C. This technology is still in early development, but one of the promising aspects of HTEL is its potential for integration with thermal power plants or industrial processes where waste heat is available. The obtained syngas can then be transformed into hydrocarbon fuels and chemicals, fully aligning this process fully with circular economy principles; however, there are many challenges in the development of SOECs, including finding components with high chemical and physical stability at elevated temperatures, in both reducing and oxidizing environments and under varying ionic concentrations, to avoid a decline of their integrity and conductivity in extreme conditions.

1.5 Ammonia: a carbon-free hydrogen carrier

To increase mass capacity, hydrogen is often stored as a compressed gas at pressures as high as 70 MPa or as a liquid at -253 °C; both of those methods require intensive energy consumption. Recent years have seen the development of new storage methods that make management and transportation easier: (i) physisorption storage in porous materials, such as metal organic frameworks (MOFs) and porous organic polymers (POPs); (ii) storage in metal hydrides, like LiBH₄ and MgH₂; (iii) storage in chemical hydrides, such as ammonia (NH₃), methanol (CH₃OH), and other liquid organic hydrogen carriers (LOHCs).

Between these compounds, chemical hydrides are the carriers with higher energy densities and mature transportation networks, while also being materials from which hydrogen can be more

easily released.^[38] Among them, ammonia is a promising candidate thanks to its high hydrogen content (17.6 wt%) and potential economic benefits for energy production.

In nature, nitrogen can be found in various organic and inorganic forms: N₂, the major (78 %) component of atmospheric air, contains more than 99 % of the nitrogen that exists globally. Because of its chemical inertness, most organisms cannot access atmospheric N₂; it has to go through a process called nitrogen fixation, that transform molecular nitrogen into a much more reactive compound, like NH₃ or nitrates, by breaking the triple bond N≡N and substituting it with one between N and O, H or C.^[39,40]

The reduction of N₂ to NH₃ happens through an exothermic reaction (N₂(g) + 3H₂(g) → 2NH₃(g), ΔH_{298K} = 92.2 kJ mol⁻¹), but it cannot take place spontaneously under ambient condition because of nitrogen's strong triple bond energy (941 kJ mol⁻¹), high ionization energy (15.85 eV), and poor proton affinity (1.90 eV).

Ammonia can be used as a carbon-free alternative to fossil fuels because its only by-products are nitrogen and water. It liquefies at a low pressure of 0.86 MPa at 25 °C, providing a volumetric energy density that is twice that of compressed hydrogen at 70 MPa (10.5 vs 5 MJ L⁻¹). Being the second most produced inorganic chemical in the world, with a global capacity of ~230 Mt per year, ammonia is also well-established in terms of production, easy handling, and transportation infrastructures.^[41] There are still some challenges to overcome, such as safety concerns regarding ammonia's toxicity and corrosivity, and the additional steps required to release H₂ from NH₃, which can reduce the overall efficiency; however ongoing research and development is focused on addressing these challenges to make ammonia a better hydrogen carrier.

As mentioned, storing renewable energy in the form of chemical fuels is deemed a pragmatic approach for both short- and long-term storage, especially in the transportation sector. In this regard, NH₃ has been recommended as a more technically feasible option than CH₃OH due to its more suitable chemical properties. The gravimetric H₂ content of NH₃ is 40% higher than that of CH₃OH

(17.6 vs 12.5 %wt), while the volumetric energy density is comparable (12.7 vs 15.5 MJ L⁻¹). The perk of methanol is that it's already liquid at ambient conditions, but ammonia can be conveniently liquefied at ambient temperature and a pressure of 0.86 MPa, or at atmospheric pressure with a cooled-down temperature of -33.4 °C. With a volumetric energy density of 12.7 MJ L⁻¹, NH₃ vastly outperforms liquid hydrogen (8.49 MJ L⁻¹) and compressed gas (4.5 MJ L⁻¹ at 69 MPa and 25 °C), other than being completely carbon-free.

One of the primary limitations of ammonia is its apparent toxicity, which is approximately three orders of magnitude greater than that of methanol or gasoline.^[42] To ensure safe use of ammonia, recommended exposure limits are set below 100 ppm: it's possible to monitor potential NH₃ leaks in real-time using appropriate sensors, but also the human nose can detect ammonia at concentrations as low as 5 ppm in air, making it much more noticeable than odorless hydrogen. Also, gaseous ammonia is less dense than air at ambient conditions, with a density of 0.769 kg m⁻³ (while air density is 1.225 kg m⁻³), making it easier for it to dissipate quickly under atmospheric pressure conditions and reducing the risk of fire or explosion in the event of a leak. Additionally, the flammability range of ammonia is narrow, ranging from 15.2% to 27.4% in dry air and from 16% to 26.6% in 100% relative humidity air, when compared to hydrogen. Ammonia has a higher automatic ignition temperature of 650 °C compared to hydrogen's 520 °C, indicating a lower risk of fire.

1.6 Commercial ammonia production

The most common nitrogen fixation is biological nitrogen fixation: N₂ is a fundamental building block of nearly all biomolecules, and thus it's essential for organisms to survive and grow. As said above, nitrogen is kinetically inert, and most organisms can't directly metabolize it; prokaryotic organisms (such as rhizobia, fishy algae, and nitrogen-fixing screw bacteria) can reduce, under ambient conditions, N₂ to NH₃, producing metabolically-usable forms of nitrogen and making them available to other organisms, using, as the only energy input, renewable solar light. This

biological process takes place thanks to the nitrogenase enzyme system: consisting of two metalloprotein (a Fe one and a MoFe one), it catalyzes not only the reduction of molecular nitrogen to ammonia, but also the reduction of protons to hydrogen and of other substrates like acetylene, azide and cyanide.^[43]

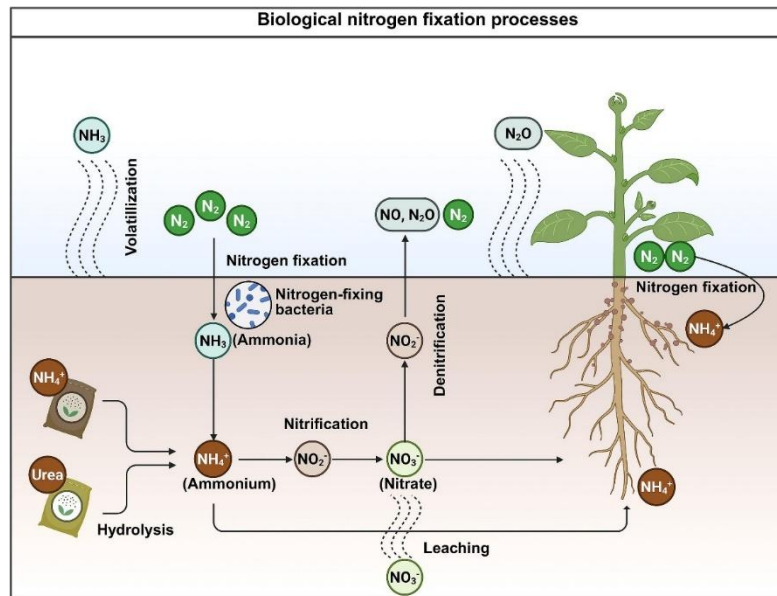


Figure 4. Schematic overview of major nitrogen transformations in biological nitrogen fixation processes. Nitrogen enters the agroecosystem mainly through biological nitrogen fixation and nitrogen fertilizer application. NH_3 converts to NO_3^- via nitrification, and NO_3^- can convert to N_2 by denitrification. Nitrification and denitrification produce the greenhouse gas N_2O . Meanwhile, NH_3 can volatilize and NO_3^- may leach, causing pollution. Plant biological nitrogen fixation also affects nitrogen transformations in the rhizosphere. Copyright 2025, Elsevier⁴⁰

Historically, many attempts have been made to achieve artificial nitrogen fixation, like the Haber-Bosch (H-B) process, the Franck-Carlo method and the Birkland-Eyde process. Among these, on an industrial scale, ammonia is still mainly produced using the H-B process, developed by Fritz Haber and commercially implemented by Carl Bosch in the early 1900s: following a dissociative pathway, gaseous hydrogen (H_2) and gaseous nitrogen (N_2) react, typically over a Fe-catalyst, at high pressure (above 200 atm) and temperature (above 400 °C).^[44] Despite the conversion rate of a single reaction being only 15 %, recycling the unreacted gases ups the total conversion rate to 97 %. Over the years, the process has gone through various improvements like switching from coal gasification

to steam methane reforming as the source of H_2 , catalysts technological advancement, improved heat integration, etc. Through these optimizations, the energy used has been reduced to 0.48 MJ mol^{-1} of generated ammonia; the most energy-consuming aspect remains hydrogen generation via the thermal and catalytic cracking of fossil fuels and it's improbable that technologically improved catalyst could enhance the energy efficiency of the process.^[45,46]

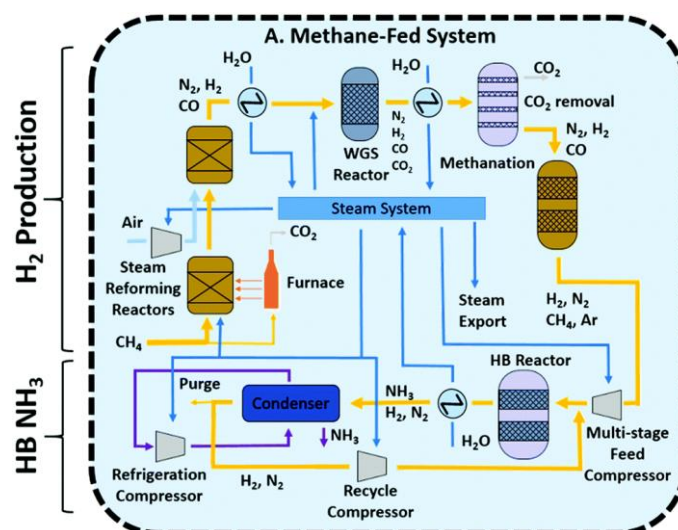


Figure 5. Schematic diagram of a typical conventional methane-fed Haber-Bosch process. Copyright 2019, RSC⁴⁶

The harsh conditions needed for the thermo-catalytic reaction to happen and natural gas used as H_2 feedstock are the biggest obstacles when considering to introduce ammonia in a cost-effective and sustainable economy: the H-B process accounts annually for 2% of the global energy consumptions and for the emission of more than 300 million metric tons of CO_2 , considering that carbon dioxide is released both by the ammonia synthesis and the natural gas extraction. An implementation of environmentally friendly and cost-effective synthetic processes for industrial ammonia production is thus needed to move us forward to a low-carbon sustainable economy.^[39]

2. Photocatalysis: harnessing the sun in the production of hydrogen and ammonia

The solar energy reaching the Earth per year is 3,400,000 EJ, and the corresponding total solar flux is equal to 1.08×10^8 GW. At the distance of the Earth from the Sun, the solar constant is 1367 W m^{-2} , and as a consequence of the absorption and scattering of the radiation from the atmosphere, the year/day-averaged energy density at the Earth's surface falls down to 170 W m^{-2} .^[47]

The impressive amount of energy reaching our planet as electromagnetic energy from the Sun is the real fuel of the Earth; it's at the basis of all of the most important cycles (e.g., hydrologic cycle) and processes allowing the existence of highly evolved forms of life on the Earth's surface. The overall primary energy consumption of the human population is estimated roughly as 6000 GW, nearly three orders of magnitude lower than the amount of solar energy that reaches the Earth's surface.^[48]

Conversion of light reaching the surface into chemicals through the photosynthetic process is the bedrock on which the development of superior organisms stands. It has also contributed to the overall definition of the atmospheric composition.

The first systematic and scientific investigation of the chemical processes activated by sunlight was dated 1777, by the studies of the Swedish chemist C. W. Scheel; he described the violet-light-activated reduction of silver chloride to metal silver. The first principle of photochemistry was defined by the pioneering works of T. von Grotthuss (1817) and J. W. Draper (1841), who established that only absorbed light is effective in producing photochemical change (the so-called Grotthuss–Draper principle).

The idea of carrying out the photochemical process in the presence of a photocatalytic material was proposed at the beginning of the 20th century^[49,50], but only in the 1940s, the

photocatalytic properties of oxides were discovered and investigated; that was often done with the objective of increasing the life of paints, papers and textiles containing TiO_2 or other white semiconductors, used as pigments.

Especially in the first part of the 20th century, the term “photocatalytic reaction” was often used with a more general meaning of “photochemical reaction”, because no catalyst was added in the reaction medium to accelerate the kinetics of a process. A photocatalytic reaction is deemed such only in “the presence of a substance—the photocatalyst—that absorbs light and is involved in the chemical transformation of the reaction partners”; furthermore, the photocatalyst must regenerate its chemical composition and properties after each catalytic cycle. ^[51]

Only from in the 1970s, with the seminal works by Fujishima and Honda on the photo-assisted electro-splitting of water on TiO_2 electrodes^[52,53] and by Inoue et al. on the photocatalyzed reduction of CO_2 on irradiated semiconductors^[54], the investigation in the photocatalytic process started to turn toward environmental remediation and the field of energetics.

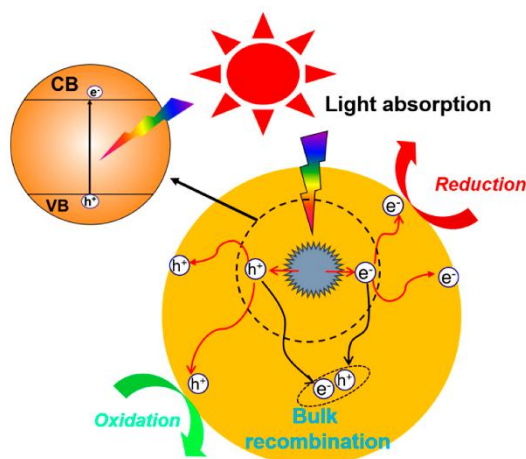


Figure 6. Simulation of semiconductor photocatalysis under light irradiation. Copyright 2018, MDPI⁵³

The groundbreaking discovery of the Fujishima-Honda effect – under UV (ultraviolet) light, TiO_2 can split a water molecule into H_2 and O_2 – highlighted another sustainable method for the production of green hydrogen: the only necessary ingredients are sunlight, water and a photocatalyst, usually a nanostructured semiconductor, that absorbs sunlight and, on whose surface, the water-

reduction and oxidation reactions take place. This kind of photocatalyzed reaction is essentially an artificial photosynthesis.

Similar to hydrogen, ammonia can also be synthesized through the use of a photocatalytic method called photocatalytic nitrogen fixation (PNF): PNF utilizes nitrogen and water as reagents, with sunlight as the energy source, to produce ammonia, making it both an environmentally friendly and energy-saving process. Firstly, N_2 is chemisorbed on the photocatalyst surface, where it's activated. Then the semiconductor is excited by solar light irradiation, resulting in the formation of photogenerated electrons and holes that move, respectively, to the conduction band (CB) and the valence band (VB). Finally, after migrating to the surface of the catalyst, the photogenerated electrons reduce N_2 to NH_3 , while the holes oxidize H_2O to O_2 .^[55]

And, like for hydrogen, titania-based photocatalysts were the first synthetic catalysts used in photocatalytic nitrogen fixation: as said above, in 1977 Schrauzer and Guth synthesized iron-doped TiO_2 by heating anatase TiO_2 impregnated with Fe(III) sulfate, and they found out that NH_3 yield increased compared with wet rutile TiO_2 .^[56]

2.1 Photocatalyzed water-splitting

When compared with an electrolyzer, photocatalytic systems are inherently simpler: they do not require robust electrical circuits, as the water-splitting reaction takes place within the single photocatalyst particle, or a few at most. Therefore, the reaction system can be distributed over a large area based on a low-cost solution process, and, even as the system size increases, the adverse effects of pH gradients and solution resistance are expected to be marginal. As a result, it was estimated that photocatalysts capable of splitting water with solar-to-hydrogen conversion efficiency values of 10% and lifetimes of 10 years can achieve economically viable solar hydrogen production via photocatalytic water splitting.^[48]

The solar to hydrogen (STH) efficiency of photocatalytic water-splitting depends on a series of correlated processes: light absorption, charge carrier generation & separation, transport, surface catalysis, and mass transfer. Within femto- to picoseconds after photoexcitation, the charge carriers settle in their respective bands (conduction band for electrons and valence band for holes), and then migrate to the semiconductor's surface within nano- to microseconds, where they drive the redox reactions. However narrow band gaps and short carrier lifetimes often cause the charge carriers to recombine, and the absorbed energy dissipate as heat, decreasing the hydrogen production efficiency.^[57]

Band gap energy and band edge positions are critical when choosing a photocatalyst: a minimum band gap of 1.23 eV is required to drive water redox reactions, while an optimal range of 2.0–3.0 eV ensures effective charge transport, redox activity, and solar absorption. The conduction band should be more negative than 0.0 V to enable hydrogen evolution, while the valence band must be more positive than 1.23 V to facilitate oxygen evolution.^[58]

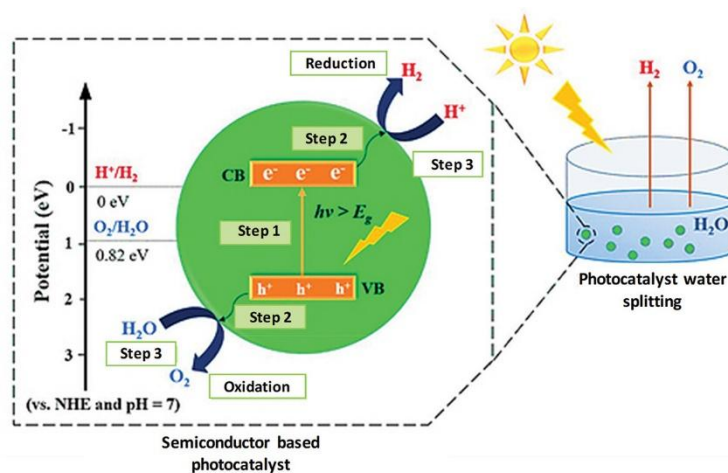


Figure 7. Representation of the mechanism of photocatalytic water-splitting over semiconductor-based photocatalyst

Recent improvements in the apparent quantum yield (AQY), visible-light response and durability of photocatalytic materials, and in the separation, recovery and application of the hydrogen gas produced (that, with oxygen gas, makes up an explosive mixture) to methanation reactions, have

shown the feasibility of safe, large-scale hydrogen production from water using particulate photocatalysts and its direct application to chemical synthesis.^[59–61] Nevertheless, there are many challenges to overcome before the green hydrogen produced by photocatalytic water splitting can be cheaply available and deliverable to users in large quantity. These include developing improved photocatalysts and gas-separation processes: STH efficiencies achieved by photocatalytic water-splitting are presently on the order of 1% at most, an order of magnitude lower than electrolyzers and photoelectrochemical cells powered by photovoltaic cells.^[62] In addition, the energy efficiency of hydrogen gas-separation methods and the recovery rate for purified hydrogen from the raw product are not yet satisfactory; a low STH efficiency and immature reaction systems mean that the cost of green hydrogen produced by photocatalytic water splitting is currently higher than that of hydrogen produced by photovoltaic-assisted electrolysis.^[63]

2.2 Nitrogen Photofixation

To be used as a PNF photocatalyst, a semiconductor's band gap should be narrow enough to utilize a broader range of the solar spectrum, while large enough to have CB energy level more negative than N_2 reduction potential and VB energy level more positive than water oxidation potential to allow both the nitrogen reduction reaction (NRR) and the oxygen evolution reaction (OER) to happen. The photocatalyst should also be, ideally, highly selective toward the ammonia synthesis, because, in protic solvents, the hydrogen evolution reaction (HER) is likely to compete with the NRR: this happens because HER requires fewer electrons.^[64]

The main drawback of this synthesis is low solar-to-chemical conversion efficiency of the majority of photocatalysts, and this is due to: (i) the strength of the triple bond $\text{N} \equiv \text{N}$, the cleavage of which is the rate-determining step of N_2 fixation, and the difficult absorption of nitrogen molecules on a catalyst surface, due to its non-polarity and saturation properties; (ii) nearly half of the full spectrum of sunlight is wasted because the majority of photocatalytic systems operate in the UV-Vis light range, while NIR (near-infrared) light ($> 800 \text{ nm}$) is rarely utilized; (iii) the high recombination rate of the photogenerated carriers, due to poor interfacial charge transfer and slow diffusion to the surface of the photocatalyst; (iv) the high overpotential of the OER delays the NRR oxidation half reaction and the reduction potential of NRR is similar, in both acidic and alkaline environments, to HER, considered thus the major competitive reaction.^[65,66] All these factors contribute to lowering the performance of photocatalytic nitrogen fixation systems under the minimum standard for large-scale production.

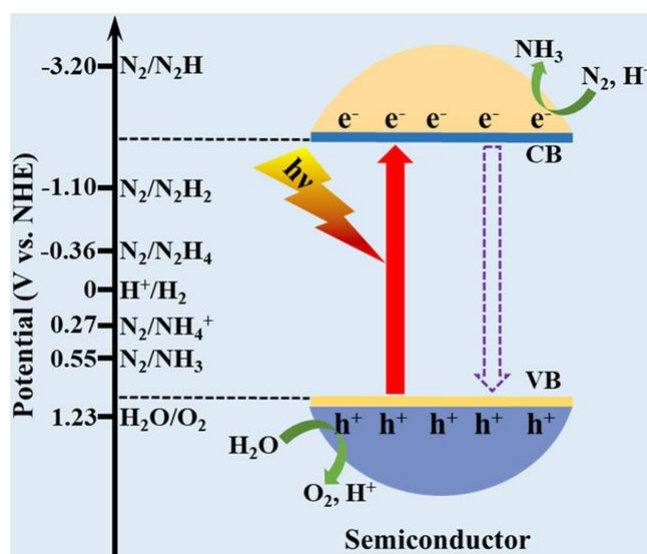


Figure 8. Equilibrium potentials (referenced to the NHE at $\text{pH} = 0.0$) of various typical NRRs via the PCET (proton-coupled electron transfer) process. Copyright 2020, Wiley⁶⁴

2.3 Photocatalytic materials: a brief history

Serpone and Emeline propose three different generations of photocatalyst, as a function of the material type: pristine semiconductors, doped semiconductors and heterojunctions^[47].

2.3.1 *Pristine semiconductors*

Binary oxides like ZnO, WO₃ and, most importantly, TiO₂ compose the first generation of photocatalysts: in 1955, Markam gave one of the earliest descriptions of the photocatalytic properties of oxides like ZnO, Sb₂O₃ and TiO₂, including the catalyzed oxidation of organic compounds under UV light. In 1972, the seminal work of Fujishima and Honda – demonstrating that water could be subjected to photocatalytic water-splitting by using in combination an illuminated TiO₂ and dark Pt electrode to yield stoichiometric quantities of H₂ and O₂ – gave start to modern heterogeneous photocatalysis with TiO₂ as the “workhorse” of the bunch.^[67]

The reasons for this choice are several: chemical stability, non-toxicity, earth abundance and low cost. Most importantly, though, the valence band of TiO₂ is more positive than E_{ox}^0 of O₂/H₂O (1.23 eV vs NHE, pH = 0) and the conduction band is more negative than E_{red}^0 of H⁺/H₂ (0 eV vs NHE, pH = 0).^[68]

The big drawbacks of TiO₂ usage are two: the fast charge carrier recombination and the inability to harvest visible-light because of the wide band-gap (3.0-3.2 eV, it covers only 5% of the solar spectrum) sported by the material.^[68] Thanks to TiO₂ structural and chemical properties, it's still possible to tune the band gap – and with it light absorption properties, recombination time etc. – by increasing the number of active sites and improving electrical conductivity. Structurally, TiO₂ can exist as one of several polymorphs: the most common ones are brookite, rutile and anatase, with the last two being the most used for photocatalytic water-splitting.^[69]

This first generation was hotly debated during the period starting from the 1980s to the 2000s: fundamental studies didn't keep the pace with applicative research, mostly for environmental uses,

(e.g. TiO_2 used in the photodegradation of pollutants), but they were still fundamental in the discovery of the mechanism of production and transfer of the charge carriers generated inside the material and into the nature of the reactive species operative in the investigated photocatalyzed processes, and they brought with them pioneering experimental approaches. The biggest question regarding these photocatalyst were i) the nature of the oxidative agent (holes versus hydroxyl radicals), ii) the sites where the reaction takes place (on the surface vs in the bulk of the material), iii) if TiO_2 really is a photocatalyst because of the difficulty in determining turnover numbers, and iv) how to improve performance and assess process efficiency.^[47,67]

Narrow band gap semiconductors like CdS (2.4 eV) and WO_3 were also part of the wider scientific investigation, but because of the serious photocorrosion CdS is subjected to ($\text{CdS} + 2\text{h}^+ \rightarrow \text{Cd}^{2+} + \text{S}$) and the relatively positive CB of WO_3 not being able to carry on the photocatalytic reaction satisfactorily, these two materials are considered inefficient photocatalyst by themselves.^[70,71]

More visible light-active photocatalyst, who have been reported in recent years, falling in this category are complex oxides like Bi_2WO_6 , Bi_2MoO_6 and BiVO_4 , nitrides like C_3N_4 ^[72], but also organic polymers^[73], MOFs and COFs (metal-organic and covalent-organic frameworks)^[74].

2.3.2 *Doped semiconductors*

To answer the question “how to improve the efficiency of the photocatalytic process?” the scientific community developed the second generation of photocatalysts: doped semiconductors. The strategy, that took center stage in the 2000s, of creating impurity levels – called color centers – in the forbidden band through ion doping derives from a desire to push the absorption onset of pristine TiO_2 toward longer wavelengths (E_g anatase $\text{TiO}_2 = 3.2$ eV, absorption onset = 387 nm). This narrowing of the band gap increases the amount of light absorbed by the photocatalyst, making it photoactive not only in the UV, but also in the visible-light region.^[67]

The 2001 study of Asahi et al. reported visible-light-active (VLA) N-doped TiO₂ triggering, together with subsequent publications, a debate on the root cause of the red shift of the absorption onset of TiO₂ to the visible region. The two most proposed answers for the corresponding increases in photoactivity were (i) a narrowing of TiO₂ intrinsic band gap or (ii) the presence of oxygen vacancies created by the doping bringing to the formation of color centers, and thus leading to the rise of the absorption bands in the visible spectral region.

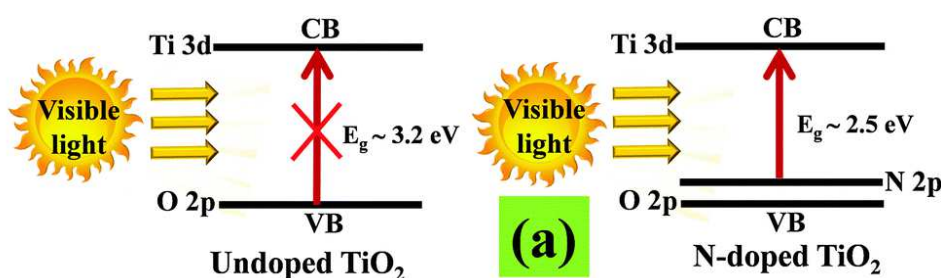


Figure 9. Energy level diagrams for undoped and N-doped TiO₂. Copyright 2016, RSC⁷⁵

Metal ion doping creates impurity levels in the forbidden band: oxygen vacancies generated by a metal cation with a different oxidation state (like Ti³⁺ in TiO₂) creates color centers, that make the wide band gap photoactive in the visible-light region.^[47,75] Non-metal dopants (C, N, S, etc.), instead of creating donor levels, tend to shift the valence band upward.

Outside of TiO₂, a great many materials were investigated, including both UV photoactive materials – like SrTiO₃ (doped with Cr, Mn, Ru, Rh,... for example), CaTiO₃ (doped with Rh and Cu), ZnS (doped with Cu and Ni) – and already visible-light active (VLA) photocatalysts like In₂O₃ (doped with C and N), CdS (doped with Cu, Zn, Ni...), ZnInS (Cu) etc.^[70] It's notable to say that a semiconductor can be co-doped, like TiO₂:(Mo+C), in which the two ions work as a charge-compensated donor-acceptor pairs.^[76]

The band structure can also be controlled by forming **solid solutions** between a wide and narrow band gap semiconductor: the band gap and the band positions can be tuned by varying the

ratio of the two semiconductors. Example of this strategy are $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ solid solutions^[77], $\text{CaMoO}_4\text{--BiVO}_4$ ^[78], BiYWO_6 ^[79] etc.

Another powerful strategy to enable visible-light harvesting in a wide gap semiconductor is **dye sensitization**^[67]. Since the breakthrough work by O'Regan and Grätzel in 1991, the dye-sensitized solar cell has attracted much attention, owing to its stability, low cost, and device efficiency. The operating principle of dye-sensitized solar cells usually involves the excitation of the dye and then charge transfer from the dye to the semiconductor: this has also been applied to photocatalytic water-splitting, e.g. Pt/TiO_2 sensitized with a polymer-pendant $\text{Ru}(\text{bpy})_3^{2+}$ complex is effective in H_2 evolution in the presence of the sacrificial donor (EDTA) under visible-light irradiation. What happens is that the photoexcitation of the dye adsorbed onto the semiconductor leads to the injection of electrons into the conduction band of the semiconductor. The electrons are consumed by the reduction of H_2O to produce H_2 . Oxidized dye molecules are subsequently reduced and then regenerated by accepting electrons from the electron donor.

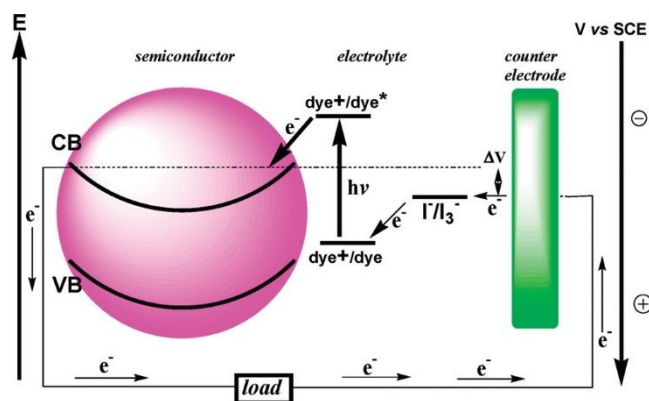


Figure 10. Schematic of the principle of the dye-sensitized (Grätzel) cell indicating different phases. Copyright 2012, RSC⁶⁷

2.3.3 Heterojunctions

In the photocatalytic process, the recombination of hole-electron pairs is an opposing process: instead of transferring to the surface of the photocatalyst, where they initiate a redox reaction, electron and holes recombine either in a radiative or non-radiative way. One of the most promising strategies applied to resolve this issue is at the center of the last proposed generation of photocatalysts, the engineering of heterojunctions..^[71]

A heterojunction is defined as the interface between two different semiconductors (S-S heterojunction)^[72] with unequal band structure: if the two semiconductors possess different Fermi energy levels (E_F), a built-in electric field is expected to form at the heterojunction interface due to the spontaneous diffusion of electrons from the semiconductor with a higher E_F to the one with a lower E_F . Under photoirradiation, non-equilibrium carriers (photogenerated holes and electrons) move between the semiconductors through the built-in electric field, consequently inhibiting their recombination.^[80]

Conventional heterojunctions are divided in three types: type-I (containing a straddling gap), type-II (containing a staggered gap) and type-III (containing a broken gap).^[81,82]

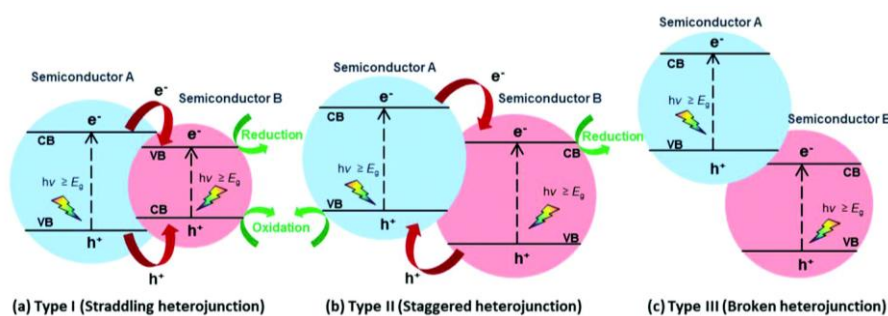


Figure 11. Schematic illustration of electron–hole pair separation in: (a) Type-I heterojunction (straddling gap), (b) Type-II heterojunction (staggered gap), (c) Type-III heterojunction (broken gap). Copyright 2021, RSC⁸²

In a **type-I heterojunction**, the conduction band (CB) of the semiconductor A is higher than CB of the semiconductor B while the valence band (VB) of A is lower than the VB of B. When

irradiated, electrons and holes accumulate in the conduction and valence bands, respectively, of the semiconductor B. This type of heterojunction is not effective in the separations of charge carriers, because they both move on a semiconductor with a lower band gap, making it easier for them to recombine. Moreover, the reaction takes place on the semiconductor with the lower redox potential: the heterojunction thus shows reduced photocatalytic ability.

Type-II heterojunctions are defined by a staggered band gap, where the CB and VB of the semiconductor A are both higher than the corresponding ones of B: photogenerated electrons will move in the CB of B, while the photogenerated holes in the VB of A, resulting in a spatial separation of the charge-carrier couples. Similarly to type-I, a type-II heterojunction will have a lower redox ability because photoredox reactions happen on the valence and conduction bands with a lower oxidation and reaction potential, respectively.

The architecture of the **type-III heterojunctions** is similar to the type-II but the staggering between the gaps is so extreme that they don't even overlap; therefore, no charge-carriers separation occurs, and the heterojunction is unsuitable for tamping down recombination.^[81]

The most effective conventional heterojunction is a type-II like $\text{TiO}_2/\text{g-C}_3\text{N}_4$ ^[83], $\text{BiVO}_4/\text{WO}_3$ ^[84], $\text{g-C}_3\text{N}_4/\text{WO}_3$ ^[85,86] and so on. Generally, they exhibit good electron-hole separation efficiency, wide light-absorption range, and fast mass transfer.

An interesting example of type-II heterojunctions used for photocatalytic water-splitting are VLA CdS/ZnO core/shell nanofibers: this type-II heterojunction significantly facilitates the electron-hole separation and the core-shell structure enhance the surface contact between the semiconductors, increasing the contact interface and the charge-carriers separation efficiency. As a result, its photocatalytic hydrogen production is higher than that of single compounds.^[87] Mou et al. constructed $\text{g-C}_3\text{N}_4/\text{ZrO}_2$ lamellar composites by a simple one-step pyrolysis of the deep eutectic solvent $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}/\text{urea}$ and then employed them in PNF, reaching an ammonia yield 7.9 times that of pristine graphitic carbon nitride, $\text{g-C}_3\text{N}_4$, and 27.5 times that of ZrO_2 . The introduction of amorphous

ZrO₂ restrains the hydrogen generation, and the amorphous ZrO₂ and g-C₃N₄ together contribute to the rapid photoproduced electron transfer of less electron–hole pair recombination.^[88] A type-II heterojunction can also be created by using two different phases of the same semiconductor: an instance of this is P25, the mixed phase of TiO₂, containing both anatase and rutile, that has been commercialized and it's widely used in various photocatalytic application. Its efficient charge separation is due to CB and VB of rutile being lower than the corresponding bands of anatase.^[81]

Type-II heterojunctions' application is limited by various factors: the first, already mentioned before, is the reduced redox ability due to the photocatalytic reactions happening on the semiconductor with lower reduction and oxidation potentials. Another is that migration of both charge carriers is physically unfavorable because of electrostatic repulsion between the electrons when they're moving from A to the electron-rich CB of B and between the holes when they're moving from B to the hole-rich VB of A.

To solve these issues, **p-n heterojunctions** are born by combining p-typed and n-type semiconductors. Before light irradiation, the electrons on the n-type semiconductor near the p–n interface tend to diffuse into the p-type semiconductor and, vice-versa, the holes on the p-type semiconductor near the p–n interface tend to diffuse into the n-type semiconductor; this means that the diffusing electrons will leave a positively charged species in the n-type semiconductor, and the diffusing holes will leave a negative charged species in the p-type one. This electron–hole diffusion will continue until the Fermi level equilibrium of the system is achieved and this movements create a charged region near the p–n interface, with an internal electric field.

Once the heterojunction is irradiated with enough energy to photoexcite the semiconductors, photogenerated electrons and holes in the p-type and n-type semiconductors will migrate under the influence of the internal electric field to the CB of the n-type semiconductor and the VB of the p-type semiconductor, respectively, which results in the spatial separation of the electron–hole pairs.

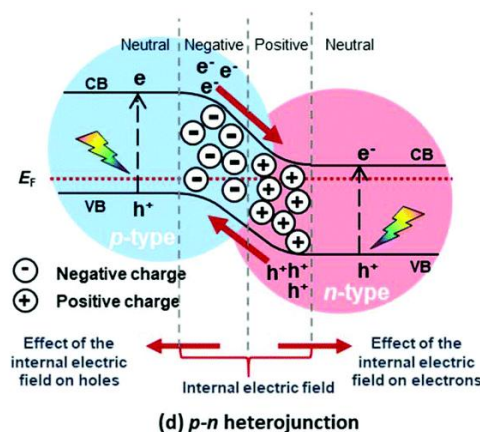


Figure 12. Schematic illustration of electron–hole pair separation in a *p-n* heterojunction. Copyright 2021, RSC⁸²

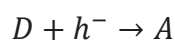
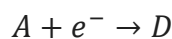
Differently than what happens for type-II heterojunctions, this electron–hole separation process is also thermodynamically feasible because both the CB and the VB of the p-type semiconductor are normally located higher than those of the n-type semiconductor in a *p-n* heterojunction photocatalyst. As a result, the electron–hole separation in *p-n* heterojunction is faster than that of type-II heterojunction photocatalysts due to the synergy between the internal electric field and the band alignment.^[81]

For example, NiS/CdS nanorods with *p-n* heterojunctions can greatly improve the photocatalytic hydrogen-production efficiency of CdS.^[89] NiS nanoparticles (NPs) were uniformly dispersed on the surface of CdS nanorods, thereby providing larger contact interface for creating *p-n* heterojunctions between NiS and CdS. The formation of *p-n* heterojunctions can facilitate charge transfer between NiS and CdS and suppress charge-carriers recombination. Meanwhile, CdS nanorods can enhance electron transport because of their one-dimensional (1D) structure. As a result, the photocatalytic hydrogen-production rate on NiS/CdS nanorods with 5 wt% NiS is much higher

than that of the pure CdS and 1 wt% Pt-loaded CdS. Zhang *et al.*^[90] combined p-type ZnMoCdS with n-type g-C₃N₄ by hydrothermal post-treatment of the two components, where the resulting composite displayed an ammonia yield 13.5-fold and 1.75-fold greater than those of individual g-C₃N₄ and ZnMoCdS, respectively, thanks to the strong electronic coupling between the two and the presence, on the ternary metal sulfide, of sulfur vacancies; these vacancies act as adsorption and activation sites for N₂ and enhance the separation of charge carriers.

Another interesting type of heterojunctions are **surface heterojunctions**: different crystal facets of a single semiconductor possess different band structure and, when coupled, show an enhanced electron-hole separation – just like a conventional heterojunction. An example is the heterojunction formed between the {001} and {101} facets of anatase TiO₂: its principle is similar to that of the type-II heterojunction, in which the CB and VB levels of the {001} facets are higher than the corresponding levels of the {101} facets. Thus, electrons and holes can be spatially separated on the {101} facets for reduction reactions and on the {001} facets for oxidation reactions. This discovery makes possible the design of heterojunction systems into the surface of single nanoparticle. In addition, only using one semiconductor slashes down fabrication costs. Notably, the redox potential loss of a type-II heterojunction photocatalyst can also be minimized by creating a surface heterojunction; even if the difference in the band structures between the {001} and {101} facets of TiO₂ is small, it also causes a overflow effect of holes and electrons, consequently reducing the charge-carriers separation efficiency. By selective deposition of oxidation and reduction co-catalysts on a semiconductor, it's possible to predetermine the type of oxidation and reduction sites: for example, Pt NPs selectively loaded on the electron-rich {101} facets of anatase TiO₂ help with enhancing the photocatalytic activity of the material. The photocatalytic hydrogen-production activity of the sample with an optimal ratio of the exposed {001} and {101} facets and 0.5% loading of Pt was ca. 9 times higher than that of the corresponding sample dominated by {101} facets.^[91,92]

To overcome the problem of the reduced redox ability of the type-II heterojunctions, **Z-scheme** type heterojunctions were introduced in 1979 by Bard et al.^[93] A conventional Z-scheme photocatalytic system is composed of two different semiconductors not in physical contact, photocatalyst I (PS I) and photocatalyst II (PS II), and an acceptor/donor (A/D) pair. During the photocatalytic reaction, photogenerated electrons migrate from the CB of the PS II to the VB of the PS I through an A/D pair via following redox reactions:



Specifically, A is reduced into D by reacting with photogenerated electrons from the CB of PS II. After that, the D is oxidized into A by photogenerated holes from the VB. Electrons accumulating on PS I, with the higher reduction potential, and holes on PS II, with the higher oxidation potential, is a testament to this heterojunction's ability of decreasing the charge-carrier recombination rate and achieving an optimal redox ability. However, conventional Z-scheme photocatalysts can only be constructed in the liquid phase, thereby limiting their application in photocatalysis.

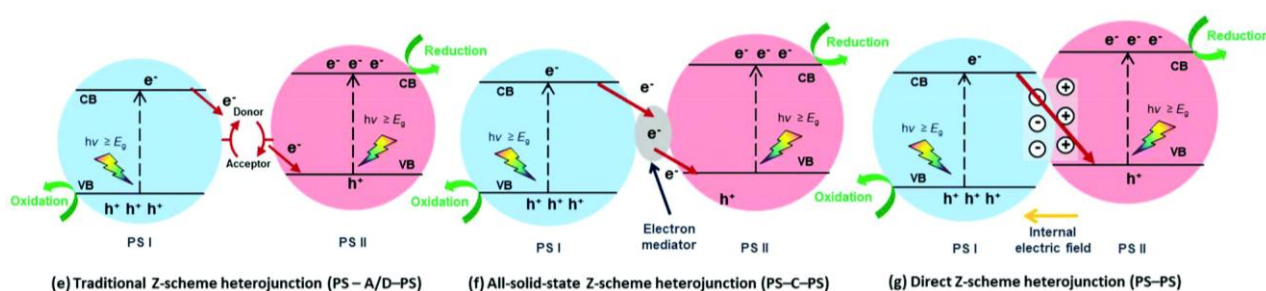


Figure 13. Schematic illustration of electron–hole pair separation in: (e) traditional Z-scheme photocatalytic system (PS–A/D–PS), (f) all-solid-state Z-scheme photocatalytic system (PS–C–PS), and (g) direct Z-scheme photocatalytic system (PS–PS) under light irradiation. Copyright 2021, RSC⁸²

An important step further came with the development of an **all-solid state Z-scheme photocatalyst** in 2006 by Tada et al.^[94] First, electrons on the VB of PS II are excited to the CB under light irradiation, leaving holes on the VB. Then, photogenerated electrons on PS II migrate to the VB

of PS I via an electron mediator (such as Pt, Ag, and Au), and are further excited to the CB of PS I. This means that photogenerated holes accumulate on the VB of the semiconductor with a higher oxidation potential and electrons on the CB of the semiconductor with a higher reduction one. An all-solid-state Z-scheme photocatalysts has a much wider application because it can be used in solution, gas, and solid media, but the electron mediators required are expensive and rare, which limits large-scale applications of these photocatalysts.

In 2013, Yu et al. prepared a **direct z-scheme photocatalyst** by coupling two semiconductors without an electron mediator.^[95] Like in solid-state z-schemes, electrons and holes are spatially separated on the semiconductor with the higher reduction potential and oxidation potential of the direct Z-scheme heterojunction photocatalyst, respectively. The fabrication cost of a direct Z-scheme heterojunction is low and comparable to that of conventional type-II heterojunction systems. Other advantages are: the optimization of its redox potential for specific photocatalytic reactions and the physically more favorable migration of photogenerated electrons from the CB of PS II to the photogenerated hole-rich VB because of electrostatic attraction between electrons and holes. An example of direct z-scheme photocatalyst is $\text{WO}_3/\text{g-C}_3\text{N}_4$ Z-scheme heterojunction used for hydrogen production under visible-light irradiation: photogenerated electrons migrates from WO_3 to $\text{g-C}_3\text{N}_4$ (reduction site, with the highest reduction potential), while photogenerated holes remain on WO_3 (oxidation site, with the highest oxidation potential) during the photocatalytic water-splitting. As a result, the photocatalytic hydrogen-production rate of $\text{WO}_3/\text{g-C}_3\text{N}_4$ Z-scheme is much higher than that of pure WO_3 and $\text{g-C}_3\text{N}_4$ components.^[96] An example of direct z-scheme heterojunction for photocatalytic nitrogen fixation is $\beta\text{-Bi}_2\text{O}_3/\text{BiOCl}$ composite: loading BiOCl nanosheets on the surface of $\beta\text{-Bi}_2\text{O}_3$ enhances the ammonia yield rate 25 times that of pure BiOCl nanosheets.^[97]

A newer type of heterojunctions has been emerging in recent years, the **S-scheme heterojunction**^[98]: an oxidation photocatalyst (OP) with lower energy Fermi level coupled to a reduction photocatalyst (RP) with a higher energy Fermi level. In the dark, electrons in RP migrate towards OP at the interface due to the energetic difference in their Fermi levels. Similar to what happen in a p-n heterojunction, OP is negatively charged and RP positively charged, leading to the formation of a built-in electric field: this results in an upward or downward bending of the conduction and valence bands at the interface of the two photocatalysts. Under light irradiation, the coexistence of the band bending and the built-in electric field makes the migration of photogenerated electrons from OP to RP easier, enhancing the photocatalytic activity of the material.

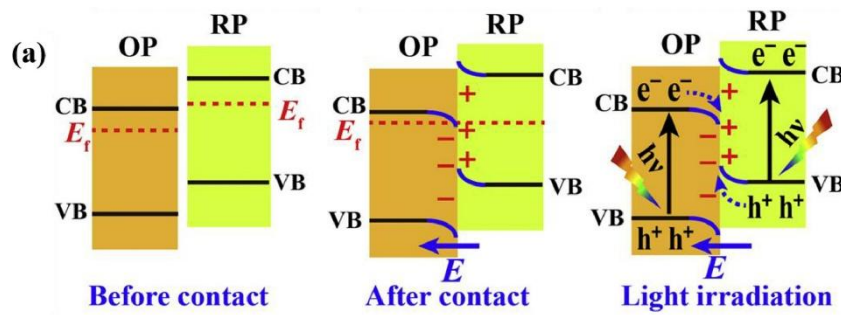


Figure 14. Mechanism of S-scheme heterojunction. Copyright 2024, Elsevier⁹⁸

When a co-catalyst like Pt is loaded onto photocatalytic semiconductor host to enhance its photocatalytic activity, what happen is akin to the formation of a **S-M heterojunction**^[72]: in this case, the formation of a space-charge separation region called Schottky barrier is enough to promote the electron-holes separation. Similar to what we have already seen for p-n and s-scheme heterojunctions at the interface of the two materials, electrons flow from the material with the higher Fermi energy level to the material with the lowest one to align them. The common build of this heterojunction is a metal coupled with an n-type semiconductor (ideally with the metal having a higher work function), where electrons will flow from the semiconductor to the metal to adjust the Fermi energy levels. The formation of the Schottky barrier results in the metal having excess negative charges and the

semiconductor excess positive ones; the Schottky barrier also work efficiently as an electron trap and prevents the charge-carriers recombination, enhancing thus the photocatalytic performance.

Interestingly, the efficiency of this heterojunction can be enhanced more by the usage of metal NPs: plasmonic metallic nanostructures are characterized by their strong interaction with resonant photons through an excitation of surface plasmon resonance (SPR). SPR can be described as the resonant photon-induced collective oscillation of valence electrons, established when the frequency of photons matches the natural frequency of surface electrons.^[99]

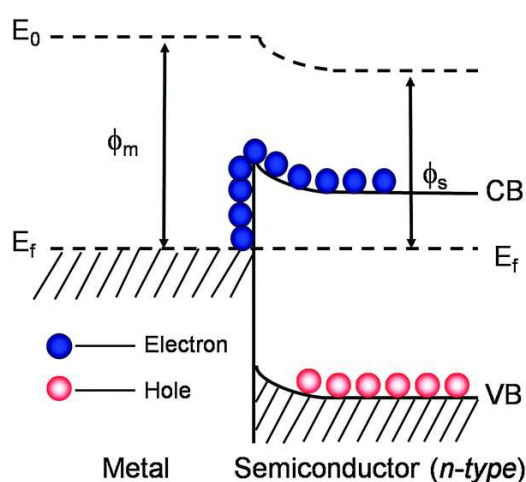


Figure 15. Schematic of the Schottky barrier. Copyright 2013, RSC⁷²

For example, gold, silver and copper nanostructures exhibit resonant behavior when interacting with ultraviolet (UV) and visible (Vis) photons. This is extremely useful in solar-light driven photocatalysis because a large fraction of the abundant solar flux consists of UV–Vis photons. The resonant wavelength and SPR intensity depend not only on the nature of the metal, but also on the size and shape of metallic nanostructures. By manipulating the composition, shape and size of plasmonic nanoparticles, it is possible to design nanostructures that interact with the entire solar spectrum and beyond.

SPR is characterized by a build-up of intense, spatially non-homogeneous oscillating electric fields around nanostructures, that is created by concentrating the light flux (the energy of incoming photons) in small volumes surrounding the particle. The spots between plasmonic nanostructures with

very high-intensity fields are often referred to as hot spots: when these surface plasmons decay, two things can happen. The resonant photons scatter radiatively in the case of larger plasmonic nanostructures (for Ag, $> 50\text{nm}$) or energetic charge carriers starts forming when the particles are smaller ($<30\text{ nm}$). These energetic carriers can be transferred to the surroundings or can relax by locally heating the nanostructure: these hot electrons can be injected directly into the semiconductor surface.

The pros of embedding plasmonic metal nanostructures in a semiconductor – instead of just loading a co-catalyst on its surface to create S-M heterojunctions – is that it partially alleviates some of the problems that affect the co-catalyst/semiconductor structure: (i) very diffuse solar flux, (ii) absorption limited to only high-energy photons in many inexpensive and widely-used semiconductors (for example, TiO_2); and (iii) large discrepancy in photon penetration depths (a few nanometers to micrometers) and minority charge-carrier diffusion length (a few nanometers) encountered by many promising semiconductors. The main consequence of this is that many energetic charge carriers are generated far from a reactive surface and recombine rather than participating in photocatalytic reactions.

3. Graphitic carbon nitride heterojunctions for solar photocatalysis

Between the many different materials used in photocatalytic application, finding ones that are stable, non-toxic for, cheap and easy to make, environmentally-friendly and particularly active when exposed to light hasn't been an easy task. A good candidate that recently emerged as a research hotspot in the field of solar energy conversion is graphitic carbon nitride (g-C₃N₄).^[100,101]

g-C₃N₄ is a non-metallic organic – consisting of earth-abundant carbon and nitrogen at a molar ratio of C/N = 0.75 – polymeric semiconductor made of tri-s-triazine repeating units with a graphitic p-conjugated structure.^[102] The earliest research on C-N compounds dates back to 1834, when Berzelius synthesized “Melon” – named as such by Liebig -, a carbon and nitrogen compound composed of heptazine structural units. In 1922, Franklin obtained an amorphous carbon–nitrogen compound by pyrolyzing mercuric thiocyanate and put forward the concept of “carbonitride” for the first time.^[103]

Its chemical inertness and insolubility in most solvents made it difficult to determine g-C₃N₄'s crystal structure: based on an 1937 X-ray crystallography study, Pauling and Sturdivant declared that a coplanar tri-s-triazine unit was the basic elementary structural unit of all polymeric g-C₃N₄ derivatives.^[104] This reported coplanar arrangement was confirmed by Leonard's group in 1982, after they successfully prepared the single-crystal structure of cyameluric derivatives (C₆N₇H₃) using a bottom-up method.^[105] In 1993, Cohen et al. simulated the structure of β-C₃N₄ and predicted its hardness to be comparable to diamond^[106] and in 1996, Teter et al. proposed five different crystal structures for carbon nitride: α phase, β phase, quasi-cubic phase (P phase), cubic phase (C phase) and graphite phase (G phase) based on theoretical calculation, with band gaps ranging from 5.5 to 2.1

eV.^[107] At ambient temperature and pressure, g-C₃N₄ has the highest stability while still showcasing semiconductive properties.

The first application of g-C₃N₄ in a visible-light-driven photocatalytic process was by Goettmann et al. in 2006, for the activation of benzene in sustainable Friedel-Crafts reactions.^[108] 2008 marks the first time g-C₃N₄ was used as the photocatalyst in a water-splitting reaction under visible light: Wang et al. found that g-C₃N₄ displayed encouraging photocatalytic activity under visible light irradiation – a milestone in the research of metal-free organic photocatalysts.^[109] Compared with more traditional inorganic semiconductors, g-C₃N₄ has many advantages: good chemical stability, tunable electronic band structure, n-type semiconductor features, earth-abundant and so on.^[110]

3.1 Structural and physicochemical properties of g-C₃N₄

Pure bulk g-C₃N₄ is a pale-yellow powder; its absorption band edge is centered around 475 nm and can be slightly altered through different synthetic methods and conditions (i.e. chosen precursor and calcination temperature). Additionally, the conjugate C-N structure endows the semiconductor with a fluorescence emission's peak at around 470 nm and a lifetime in the range of 1-5 ns. Just as for the light absorption band, its fluorescence band also changes with the preparation strategy and depends on the thickness of the material: the fluorescence quantum yield of g-C₃N₄ prepared by traditional thermal condensation is less than 5%, and the bulk needs to be stripped to form ultra-thin nanosheets (NSs) to have applicable fluorescence properties.^[102,109]

g-C₃N₄ presents a graphite-like layered structure: the layers made of aromatic heterocycles and the Van der Waals (VdW) forces binding them together are the reason for its chemical and thermal stability. The material is stable until 450°C when in an inert atmosphere, and the temperature can go as high as 600°C before it starts to decompose in air.^[111]

This graphite-like layered structure also endows g-C₃N₄ with an extremely large specific surface area, calculated to be as high as 2500 m² g⁻¹ for an ideal monolayered sample.^[102,112]

X-ray diffraction patterns show two typical XRD peaks located at 13.0° and 27.4° : the former is caused by the in-plane repeated units (separated by a distance of about $6.81 \text{ \AA}$) and the latter by the graphitic interlayers ($3.26 \text{ \AA}$)^[102]. The relative positions of C and N atoms can only be predicted through theoretical calculation and the exact stacking position are still not clear: there are two types of basic structural units, the triazine ring (C_3N_3 or s-triazine, ST, forming a $R3m$ crystal structure) and the heptazine ring (C_6N_7 , also called tri-s-triazine or TST, crystallizing in a $P6m2$ spatial group). These two structures display different energy states on account of the different sized N vacancies and variable chemical environment around nitrogen atoms: it's generally believed that g- C_3N_4 is composed of C_6N_7 units, because Kroke et al. found – through density functional theory (DFT) calculations – that the binding energy of the heptazine unit is lower than that of the triazine one, making more stable a structure composed by the former; in particular, TST units form the thermodynamically most stable configuration by generating a six-fold cavity from three heptazine rings. This structural motif is the core building block of the g- C_3N_4 network^[107,113]

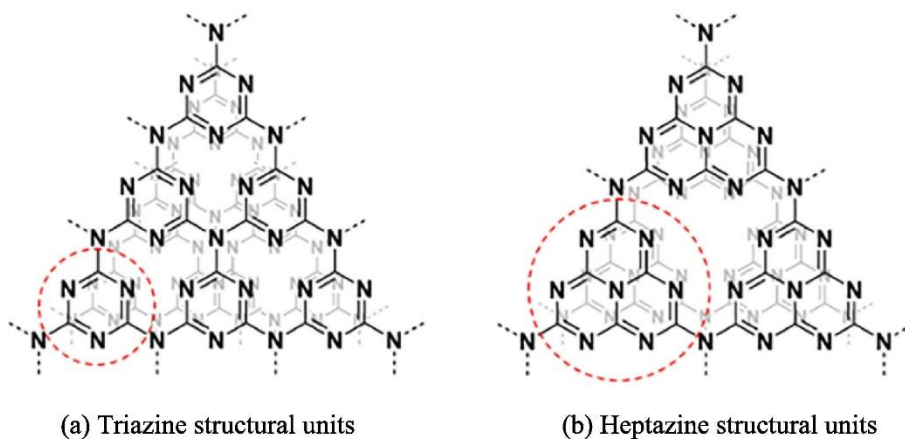


Figure 16. Two basic structural units of g- C_3N_4 . Copyright 2024, Elsevier.¹⁰²

As said before, C and N atoms are distributed in one plane and form hexagonal structures through σ bond, while the lone-pair electrons in the p_z orbitals form a highly delocalized π -conjugated framework thanks to sp^2 -hybridization: the planar units stack into infinite two-dimensional sheets through π - π interactions, while adjacent layers are held together by weak Van der Waals forces with an interlayer interaction energy of $\sim 0.036 \text{ eV}$.^[107,109,114]

This framework is believed to be responsible for g-C₃N₄'s photocatalytic reactivity: N lone-pair electrons dictate the valence band edge, while both N and C contribute to the conduction band edge. The bandgap decreases from 3.5 eV to 2.1 eV with the thinning of g-C₃N₄ NSs (going from several layers to a singular one). g-C₃N₄'s exact band gap, about 2.7 eV, can be determined through its UV-Vis Absorbance spectrum and its sufficiently large to overcome the endothermy of the water-splitting reaction: N-atoms on the valence band (VB) edge exhibit dual catalytic roles in oxidation and reduction processes, whereas the conduction band (CB) atoms participate exclusively in reduction reactions.^[107]

There are also photocatalytic disadvantages to this layered heptazine structure: interlayer π - π interactions, stabilized by N lone-pairs, hinder charge transport between different units. Localized photoexcited carriers can't be easily separated and tend to recombine. Additionally, because of the narrow interlayer spacing of the bulk form (~ 3.2 Å), mass movement is hindered and the access to active sites restricted.^[115]

These structural limitations can be overcome by exfoliating g-C₃N₄ into nanosheets or by designing porous architectures, thereby increasing surface area, facilitate charge separation, and maximizing active site accessibility.

3.2 Preparation of g-C₃N₄

Differently from more conventional photocatalysts, the synthesis of g-C₃N₄ employs cost-effective, non-toxic, and readily accessible precursors, and is generally made up by straightforward one-step procedures. The chosen precursor significantly influences the optical and electronic properties of g-C₃N₄, because different starting materials yield distinct microstructural configurations, while the impurities they contain often introduce structural defects.

Preparation methods fall broadly into two categories: physical and chemical. Physical methods are generally used to produce g-C₃N₄ films or bulk powders, using techniques such as ion implantation and mechanical ball milling. The majority of g-C₃N₄ is synthesized via chemical approaches, including solvothermal synthesis, electrochemical deposition, solid-phase reactions, thermal polycondensation, and related methods: these are considered “bottom-up” methods, because they work by polymerizing N-rich precursors – urea, cyanamide, dicyandiamide, melamine, thiourea etc. – to create the organic framework. “Top-down” methods are mostly used for exfoliating the bulk material into g-C₃N₄ nanosheets^[102,107]

The precursors of a **solvothermal synthesis** are added with an organic solvent into a high-pressure steel reactor and then heated up to a specific temperature. The g-C₃N₄ synthesized exhibits lower crystallinity when compared to thermally condensed counterparts, but this method’s useful for producing tailored morphologies and nanostructures, thanks to its mild reaction conditions, ease of operation and control of the product uniformity. An example of this is the synthesis of nanotubular g-C₃N₄ made with melamine and salicylic acid as the solvent by Jia et al.^[116]

Electrochemical deposition is the technique of choice for synthesizing g-C₃N₄ thin films, owing that to its operational simplicity, speed, and capability to process materials at relatively low temperatures. Under the influence of an electric current, a carbon-nitrogen rich organic solution is gradually deposited onto the electrode surface, forming a layer of g-C₃N₄ film. The composition of the solution (e.g. the ratio of the precursors) affects the composition of the catalyst, including the chemical bonding states of carbon and nitrogen and the evolution of the crystal structure.^[117]

The **solid-state reaction** method is similar to the solvothermal method, but it bypass the use of an organic solvent; this lack of solvent means that reaction conditions are harsher and that the obtained product usually presents graphite carbon impurities.^[118] And, similarly to electrochemical deposition, C- and N-based organic compounds are used as raw precursors in **vapor deposition** without using an organic solvent: they are decomposed into small molecules and then polymerized

into g-C₃N₄ thin film with a smooth and uniform structure, making it an important tool for in-situ growth of g-C₃N₄ on other semiconductor substrates.^[119,120]

The method we are mostly interested in is **thermal condensation**: g-C₃N₄ is easily prepared through polycondensation of precursors like melamine, dicyandiamide (DCD) and urea. The heating temperature of the process affects the structure and the photocatalytic performance of the graphitic carbon nitride: it can affect the ratio of C/N (consequently modifying E_g), and the polymerization degree, enhancing the delocalization of electrons in the aromatic sheets (better reaction temperatures make stronger VdW interactions between TST cores).^[121,122] Heating time can also affect the graphitic carbon nitride by modifying the layer thickness (the longer the isothermal step, the thinner the layers).^[123] Thermal condensation can also be done in tandem with a template or an acid treatment to obtain g-C₃N₄ with special structures and morphologies: like Zhang et al., who were able to fabricate belt- and ribbon-like bundles of g-C₃N₄ by pre-heating HCl and alcohol with melamine.^[124] Thermal condensation presents many attractive advantages: it's a simple and cost effective synthesis with high production yield, and can be easily scaled up. On the other hand, the photocatalytic properties of g-C₃N₄ fabricated via direct pyrolysis of N-rich precursors are weak, because the high reaction temperatures form many intermediates that are difficult to remove due to incomplete polycondensation: the resulting disordered structure brings to a fast recombination of the photogenerated carriers.^[125]

The traditional **thermal** and **solvothermal** synthesis usually endow g-C₃N₄ with a loose 2D or bulk morphology, while the procedure used in **deposition** strategies can control film thickness and morphology on the substrate. Once graphitic carbon nitride has been prepared in his bulk form, many different **exfoliation strategies** can be used to produce g-C₃N₄ nanosheets (monolayered or with a low layers number): chemical, thermal, ultrasonication assisted liquid exfoliation and so on.

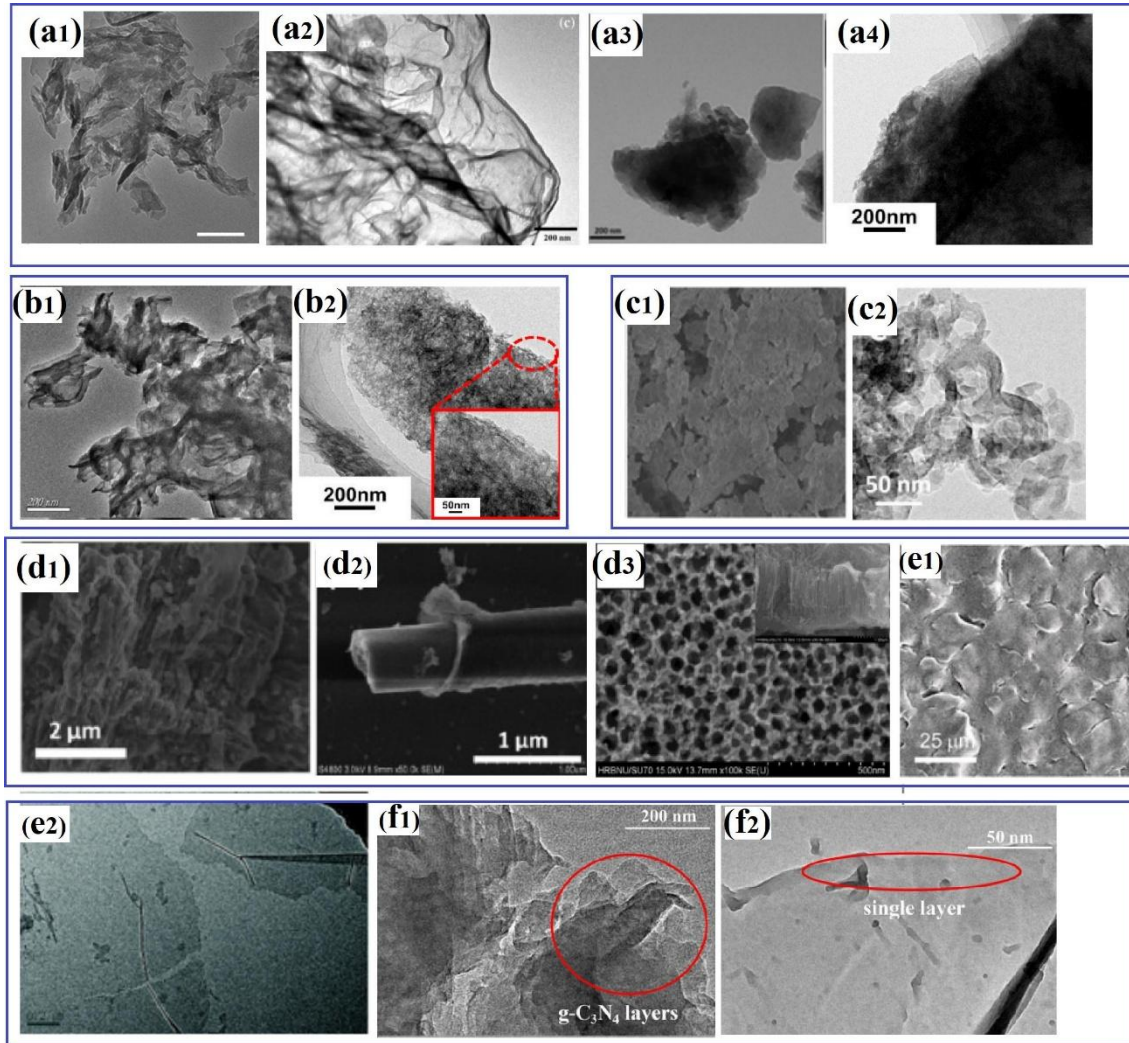


Figure 17. Morphology of g-C₃N₄ prepared by using (a) Thermal condensation polymerization method. (b) Solvothermal method (c) Solid-phase reaction method. (d) Vapor deposition method. (e) Electrochemical deposition method. (f) Exfoliation method. Copyright 2024, Elsevier.¹⁰²

3.3 Modifying g-C₃N₄

The photocatalytic efficiency of bulk g-C₃N₄ is still far away from what's required for practical applications because of:

1. Low efficiency, because of fast charge-carriers recombination;
2. Few active sites that are hard to reach, because of the low specific surface area;
3. Insufficient Vis light response, because of insufficient Vis light absorption;

4. Poor electrical conductivity, high exciton binding energy and low quantum efficiency because of the inadequate expansion of the π -conjugated system.

While redox reactions are directly affected by environmental factors (pH, temperature, the amount of photocatalyst used) that can definitely be optimized, finding a way to improve the inherent efficiency of a material is a necessary step in the direction of large-scale technological applications.

Its photocatalytic performance can thus be improved by: (i) expanding the light absorption range to increase the numbers of photogenerated charge carriers, (ii) accelerating charge migration and separation to avoid charge-carriers recombination, (iii) increasing the number and exposure of active sites to lower the energy barrier of the reaction, (iv) improving the photo-stability of the photocatalysts by inhibiting photo-corrosion.

Many strategies have been proposed to perform these improvements on the photocatalytic activity (defect engineering, surface modification, size and morphology control, co-catalyst deposition, usage of the material in heterojunctions etc.) and can be divided into two macro-groups: self-modification and exogenous modification (introduction of an assisting material).^[102]

3.3.1 *Self-modification*

When we talk about self-modification of g-C₃N₄, we mean changing the inherent properties of the material by modifying morphology, crystal phase, crystallinity, shape, size, spatial structure, surface structure and defects.

Molecular structure regulation can be used to modify charge transfer in the π -conjugated system: adjusting chemical composition and the local structure of g-C₃N₄ at a molecular level helps regulating its electronic band structure, light-absorption capacity, photoelectrical characteristics and charge-separation efficiency. This can be done through **molecular doping**: introducing small molecules during the copolymerization process makes it possible to embed target monomers with different chemical composition in the organic network. An example is the fabrication of a

nitrobenzene inarched g-C₃N₄ nanotube photocatalyst by Jiao et al.^[126]: grafting a nitrobenzene in the triazine ring enhances the system conjugation and the electron delocalization, helping with the separation of photogenerated electron and holes. The introduction of the nitrobenzene ring also narrows the band gap from 2.7 to 2.5 eV, increasing H₂ production yields by 11.2 times. **Ion doping (metal and non-metal)** is similar, but works by introducing lattice defects, thus changing the band structure: impurities creates new energy level in the electronic band structure, broadening the absorption spectrum or inhibiting charge recombination. The most commonly studied metal ions are alkali earth metals (Na, K) and transition metals (Fe, Cu, Co, Mo), and doping can be easily done by calcinating together C and N precursors with metal salts: an example of this is Jiang et al. comparing non-doped g-C₃N₄ with Li, Na and K-doped g-C₃N₄.^[127] This type of doping results in narrower band gaps with more positive VB and less negative CB positions, indicating more efficient visible light utilization and photoexcitation efficiency: as a result, doped samples display a much higher H₂ production. The use of metal ions comes with drawbacks like a high cost, contamination and poor thermal stability. Non-metal doping (C, N, P, S, B and X) has been proved to effectively improve photocatalytic activity, like for Ran et al.^[128], P-doped g-C₃N₄ nanosheets presents mid-gap states that works as electron capture centers to increase separation and transport efficiency of photogenerated electrons.

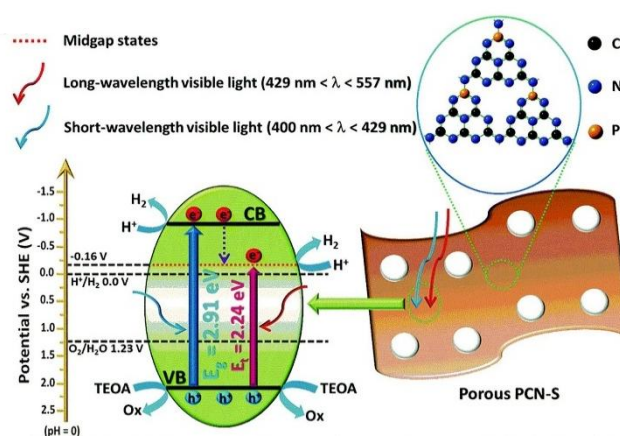


Figure 18. Photocatalytic H₂-production mechanism of porous PCN-S. Copyright 2024, Elsevier¹⁰²

In recent years, researchers have been focusing on the co-doping of g-C₃N₄ with metallic and non-metallic ions: S/K-co-doped g-C₃N₄ displayed a 98 times higher hydrogen evolution rate than pristine g-C₃N₄.^[129] Co-doping brings up a synergistic effect that expands the light-absorption region and enlarges the exposure of specific surface area and active sites, the separation of photogenerated charges, and optimizes the photoreduction potential. Co-doping is an easy way to modify the molecular structure of pristine graphitic carbon nitride: both functional groups and metallic/non-metallic ions can be introduced through simple thermal polymerization or co-polymerization, where the precursor reacts with the target dopant.

3.3.2 Defect engineering

Defects are essential for photocatalysis because they provide active sites for that reaction to happen and efficiently expand the visible light absorption range through the addition of defective energy levels in the band gap. Defects also serve as trapping sites to suppress the recombination of electron-hole pairs, improving their use in the process.^[130] This modification prevents the introduction of impurities, that, in the long run, can affect the durability of the photocatalyst. The distribution and type of defects added in the structure have a direct effect on the photocatalytic hydrogen evolution: carbon vacancies^[131], nitrogen vacancies^[130], decoration of O atoms in the N vacancies^[132] can be used to manipulate the intrinsic structure of g-C₃N₄.

Defect engineering affects the bands structure of g-C₃N₄, but also reaction dynamics by increasing the exposure of active sites, facilitating the adsorption and desorption process of intermediate H*, as well as introducing electronegative functional groups (-OH, -COOH, -OCH₃ and -NH_x) that modify the local electron distribution and improve charge separation efficiency. Introducing defects and impurities can also induce the formation of new charge recombination traps, resulting in a decreased photocatalytic hydrogen yield. It's imperative to choose carefully the preparation method: optimizing the concentration and distribution of dopants and defects is required to minimize their negative effects on photocatalytic hydrogen evolution (PHE).^[133]

3.3.3 Microstructure optimization

The microstructural regulation of g-C₃N₄, mostly done by multi-dimensional design and the introduction of porous structure, is an easy way to increase the specific surface area and the number of active sites. The morphology and the size distribution of g-C₃N₄ particles can modify the photocatalytic performance of the material: multi-dimensional structure design endows graphitic carbon nitride with different physical and chemical properties, tuning the way photogenerated carriers are made and used during the photocatalytic reaction.

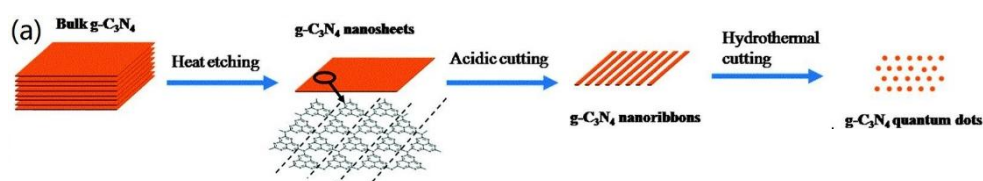


Figure 19. Schematic illustration of the controllable synthesis of g-C₃N₄ NSs, nanoribbons and quantum dots. Copyright 2024, Elsevier¹⁰²

0D nanostructures are usually quantum dots ranging from 1 to 10 nm: the diminutive size of the single nanoparticle brings with it an increased relative surface area and an outstanding number of active sites. Additionally, their smallness makes it easy to combine them with other materials or to load them in special structures. Thanks to the quantum size effect, 0D nanostructures displays characteristic light absorption and optical emission different from that of bulk materials.^[134–136]

Both “top-down” (thermo- or electro-chemical etching of bulk g-C₃N₄) and “bottom-up” (microwave-assisted or low T solid state strategies) can be used to prepare 0D nanostructures.^[136]

1D nanostructures work as fast conduction channels for photogenerated charge transport and the material’s photocatalytic performance can be optimized by tuning the nanostructures’ length and diameter. g-C₃N₄ nanorods, nanowires, nanotubes and nanoribbons are more efficient photocatalysts than bulk g-C₃N₄^[131,137–139]: e.g. Zeng et al.^[138] fabricated 1D porous architectural g-C₃N₄ nanorods

(NRs) by calcinating hydrous melamine nanofibers. The thermal treatment inserts O impurities in the graphitic structure, forming oxygen-doped g-C₃N₄: the doped material presents a decreased light absorption and a modified VB position (from +1.68 to +1.85 eV). Despite being a weaker light absorber, O-g-C₃N₄ NRs shows a vastly increased H₂ evolution yield, when compared with bulk g-C₃N₄: the improved photocatalytic performance is caused by the much higher surface area of porous NRs and the higher number of accessible active sites, as well as the easier interfacial movements of photogenerated charges along the length of the rods that dramatically accelerates axial charge transfer.^[140]

The fabrication of **2D nanostructures** is a research hot-spot for 2D layered materials and has been widely studied for photocatalytic hydrogen evolution.^[141–148] The graphene-like structure of g-C₃N₄ displays strong interlayer Van der Waals forces that induce the stacking, effectively diminishing the specific surface area of the material (less than 10 m²/g) and accelerating charge carrier recombination^[143,145,149]; when thinned out to form nanosheets (NSs), the original aromatic heterostructure is retained, with π - π conjugation contributing to the quick in plane transfer of electrons, and the 2D structure significantly shortens the distance photogenerated charges have to traverse to reach the surface. Similarly to 0D materials, a 2D nanostructure provides abundant active sites, enhancing light harvesting and reactants' adsorption.^[145–148] Both multi- and mono-layered g-C₃N₄ nanosheets have been successfully prepared by peeling the bulk material (through physical and/or chemical methods) or by using two-dimensional templates: for example, Qu and al.^[144] synthesized a single atomic layered g-C₃N₄ mesh (with a thickness of less than 0.5 nm) through solvothermal exfoliation of mesoporous g-C₃N₄. This fabricated g-C₃N₄ mesh displayed an energy band shifted upward compared to the bulk material, showing photogenerated electrons with improved reduction ability translated into a much higher H₂ evolution rate (8510 $\mu\text{mol g}^{-1} \text{h}^{-1}$) than every other 2D nanostructure previously reported.

3D g-C₃N₄ nanostructures keep the same merits of low dimensionality materials (high specific surface area, number of active sites and light absorption) while avoiding structural units agglomeration and providing a three-dimensionally interconnected network that enhance electron transport and ion diffusion, improving the photocatalytic performance of the material.^[150–152] Many strategies, including template and template-free methods, have been used for these syntheses: Chen et al.^[151] assembled ultrathin g-C₃N₄ nanosheets to form a 3D porous photocatalyst that successfully carried out the complete decomposition of water into hydrogen and oxygen under visible light. The interconnected framework, consisting of highly crystalline NSs, provides a quicker transfer path for charge carriers and, at the same time, prevents agglomeration of the NSs, endowing the photocatalyst with good durability of more than 100 h.

As mentioned before, a **porous structure** can play an important role in the photocatalytic process. Generally speaking, it can increase the specific surface area and the number of active sites, while also promoting the transport and diffusion of charge carriers and ions. In addition, the porous structure can reduce the light reflectance and increase the light absorption coefficient of the material because they heighten the internal scattering of the material. Moreover, some special pore structures can be used as micro-reactors to provide a chemically-uniform micro-environment to carry on a photocatalytic reaction.^[153–158] Up to now, template methods have been widely used for fabricating porous g-C₃N₄ (PCN): in a typical polymerization by thermal condensation,^[159–161] hard templates are easier to control, but corrosive reagents used in its removal are environmentally dangerous; soft templates are easier to remove but can decrease the polymerization degree of the material and can leave residue, which affect the photocatalytic activity.^[155,156,162] Template-free syntheses are therefore popular and a highly sought-after alternative in the fabrication of PCN.^[154–157]

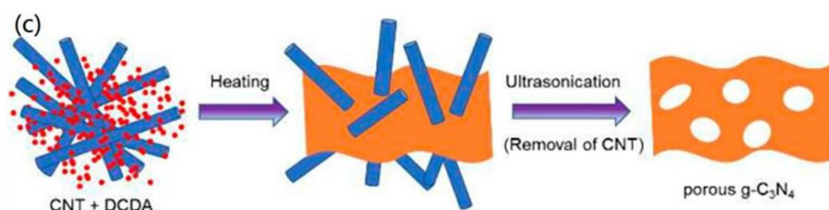


Figure 20. Schematic illustration of the synthesis of porous g-C₃N₄ using carbon nanotubes (CNT) as hard template. Copyright 2024, Elsevier¹⁰²

3.3.4 Exogenous modification

The PHE activity of pure g-C₃N₄ is limited, even after self-modification, by charge carrier recombination, insufficient active sites, slow reaction rate and competitive reactions happening at the same time; introducing a **co-catalyst** can help with reducing these problems.^[102]

By itself, the co-catalyst can be inert during the photocatalytic process, but, when coupled with g-C₃N₄, it has positive effects like suppressing charge recombination, increasing the number of active sites and reducing photo-corrosion. In other cases, the co-catalyst can also activate reactant molecules, thereby reducing the activation energy and improving the kinetics of the redox reaction, effectively increasing its efficiency^[163,164]. **Metal nanoparticles** are the most commonly used co-catalysts in photocatalytic reactions; as explained before, the formation of a Schottky barrier between the semiconductor and the metal co-catalyst eases electron-hole pairs separation and inhibits the backflow of photogenerated electrons from co-catalyst to g-C₃N₄, thus optimizing charge carrier utilization. Noble metals nanoparticles, such as Au^[165] and Ag^[166], also show SPR, further enhancing the efficiency of the material through hot electron injection. The most used noble metal-based co-catalysts in PHE contains rare metals like Pt^[167] and Pd^[168]; considering the environmental impact, low availability and high costs, their large-scale application is limited.

The PHE performance of g-C₃N₄ decorated with metallic NPs is influenced by many factors, such as amount deposited, size average, nanoparticle morphology and surface dispersion. Optimizing these factors is necessary for obtaining photocatalyst with higher efficiency: a smaller size

distribution and a bigger surface coverage are ideal, because an insufficient contact between the two materials limits the positive effects brought on by the coupling.^[102]

Decorating g-C₃N₄ with metallic NPs means creating a **heterojunction** (specifically the S-M type), more commonly formed by coupling two semi-conductive materials: g-C₃N₄ is a great building block for the construction of heterojunctions with a matched band structure and easily tunable interfacial contact, thanks to the position of its energy bands and the high structural flexibility.^[169]

As stated previously, heterojunctions usually show improved photocatalytic performances thanks the internal electric field that forms at the interface between two semiconductors: well-matched materials, in terms of band levels, lead to extended light absorption, increased number of active sites, promoted electron dissociation, and improved photo-stability^[170–172]. An example of the latter is what happens when g-C₃N₄ is coupled with photocatalysts sensitive to photo-corrosion, like CdS.

By building heterostructures, the photocatalytic optimization of the semiconductor is dramatically expanded when comparing it to self-modification strategies of the pure semiconductor. The most performance-affecting factors are the **design of the band structure** and the **control of the interface structure**: band matching between two (or more) semiconductors determines the direction toward which charge carriers move and redox capabilities of the match, the speed of exciton separation and the thermodynamic requirements needed to be met for the target reaction to happen. At the same time, improving the contact quality of the interface deeply influences the separation efficiency and transfer ability of charge carriers, facilitating their migration and improving photocatalytic efficiency.^[173]

g-C₃N₄ can form heterojunction system with most materials; different charge transfer pathways will form on the interface depending on the other material (type I, type II, Z-scheme or S-scheme etc.) and their band positions have to be suitable to carry on the target redox reaction. It's possible to optimize this process by tuning the band structure of g-C₃N₄ and selecting a matching

electron transfer mediator: Wang et al.^[174] took the g-C₃N₄/ZnIn₂S₄ type I heterojunctions and introduced defects into the graphitic carbon nitride to change its band energies. As a result, the type I heterojunctions morphed into a Z-type one, improving charge separation.

Heterostructure photocatalysts with matched band-structures can also be designed based on theoretical models provided by density functional theory (DFT): Wang et al.^[175] proved that g-C₃N₄/Ag₃VO₄ reduces the mixed electron density on the C atom and the nearby N atom by inducing electron transfer toward the Ag atom and then to the CB of Ag₃VO₄, while holes moves from Ag₃VO₄ to the VB of g-C₃N₄ to form a type II heterojunctions.

Thanks to the accelerating development of theoretical models, our understanding of composites band structures and their relationship is improving, furthering the theoretical design of band matched heterojunctions.

Another very important site of optimization is the **surface of the semiconductor**, where the photocatalytic process happens, while the carrier separation and transfer happen at the **interface between the components**. Thus, both the microstructure at the surface and at the interface directly affects the photocatalytic performance. It's imperative to design a heterojunction that optimizes both to maximize the photocatalytic efficiency of charge carriers: e.g. by controlling a semiconductor thickness and morphology, so that it can meet the requirements for light transmission depth and avoid the shielding effect. At the same time, the exposure of many highly active reaction sites on the surface should be prioritized to ensure the best possible contact between the reactant and the substrate. The surface crystal structure should also assist in the adsorption and activation of reactive molecules.^[176–179]

In the case of g-C₃N₄, 2D NS structures are helpful in exposing sufficient surface atoms with unsaturated coordination; they are effective reaction sites and, at the same time, the planarity of the material provides in situ nucleation and growth sites for the second semiconductor, promoting an intimate contact between the two materials. In addition, by introducing microporous structures on the

surface of g-C₃N₄ through a secondary treatment, new active edges can be obtained, increasing the number of active sites.

To obtain an intimately contacted interface, the bond between different materials needs to be strengthened as much as possible, so that there's less interfacial resistance during carrier transport. This can be done by regulating the **formation mode** of the interface, for example, through in-situ epitaxial growth or by building heterostructures where materials are kept together by Van der Waals forces: this method improves the transfer rate of charge carriers through a tight electronic coupling at the interface that reduces the charge transfer barrier, without needing to submit to lattice matching requirements.^[178]

Another principle to follow when optimizing the heterojunction interface is to maximize the interface contact as much as possible, so that a rich transmission channel can be set-up for fast charge transfer. Simply mixing different semiconductors is not enough: an example of optimized interface is the **core-shell heterostructure**. This heterostructure presents a larger effective area of contact, but the complete coating of the core needs to be taken in regard when considering the effective excitation of the core semiconductor: enough active sites on the surface of the core-shell structure are very important to achieve high utilization efficiency of the charge carriers^[179]. A **hollow core-shell heterostructure** can provide a solution: the intimately contacted interface between hollow core and shell layer guarantees high charge carrier separation and, at the same time, the hollow structure is not only conducive to mass diffusion and transfer, but also can cause multiple light reflection in the cavity to improve light absorption.^[180,181]

Also, **2D to 2D (2D/2D) heterostructures** make full use of the structural advantages of g-C₃N₄ to maximize the interface contact area^[182]: planar structures greatly shorten the distance of photogenerated charge carriers have to traverse from the inside of the material to the interface or to the surface reaction sites.

In conclusion, when considering the scalability and real-world application of photocatalytic technologies in the *green* production of solar fuels, it's imperative to develop efficient, low-cost, sustainable, and visible-light-driven photocatalyst. Graphitic carbon nitride, g-C₃N₄, is attracting considerable attention from the scientific community due to its high activity and efficient visible-light absorption. It contains only earth-abundant elements (carbon and nitrogen), it shows high chemical and thermal stability and a moderate bandgap energy, which can harvest the visible light as well as having suitable CB and VB edge positions. Moreover, g-C₃N₄ can be synthesized from cheap and easy to find precursors through very simple methods.

The reasons for its widespread application as a visible-light-driven (VLD) photocatalyst are many, but the photocatalytic performance of pure g-C₃N₄ is low due to its high charge-carriers recombination, low absorption coefficient, and low specific surface area: researchers are investigating many different strategies to increase the photocatalytic activity of graphitic carbon nitride. Optimizing the morphology of the material and reducing its size can increase the surface area, where the reaction happens, and decrease charge-recombination rates, by making it easier for the photogenerated carriers to move from the bulk to the surface. In addition, coupling it with other materials to build heterojunctions is an easy way to increase the amount of light harvested and to slow down charge recombination, thanks to the increased spatial distance between the oxidation and reduction site.

As research in the field increases, it's clear that so does the researchers' interest for g-C₃N₄ as a commercially-viable photocatalyst in the production of solar fuels.

4. Aim of the Thesis

The aim of this thesis is the synthesis, characterization and applications of photoactive materials in composites containing graphitic carbon nitride, g-C₃N₄, to build heterojunction used as the photocatalyst in solar-driven hydrogen and ammonia production. Three different systems have been investigated to determine how modifying materials' features affect the photocatalytic activity of a heterojunction: components ratio, morphology, crystallinity, metal doping, are all variables that, when optimized, can enhance the photocatalytic activity of a material by increasing the number of charge carriers that migrate to surface active sites, where they take part in the redox reactions, instead of recombining in the bulk of the material. g-C₃N₄ has been chosen as the common denominator in all the heterojunctions studied in this work because of its high activity, visible-light absorption, eco-friendliness, easy and cheap synthesis, and high tunability: the many ways in which it can and has been modified make this material extremely versatile for photocatalytic applications.

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Chapter 2

Mechanistic Insight into the Nitrogen Photofixation

Reaction by BiOBr-based Heterojunctions

Giulia Giovilli,^a Francesca Merlo,^a Andrea Olivati,^b Myriam Chems,^a Andrea Speltini,^a Michele Loriso,^c Silvia Colella,^d Andrea Listorti,^e Alessandro Landi,^f Andrea Peluso,^f Antonella Profumo,^a Mirko Prato,^g Julia Wiktor,^h Annamaria Petrozza,^b Francesco Ambrosio,^{c,} Lorenzo Malavasi^{a,*}*

^aEnergy and Materials Chemistry Group, Department of Chemistry and INSTM, University of Pavia, Via Taramelli 16, Pavia, 27100, Italy

^bCenter for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, 20134, Milan, Italy

^cDipartimento di Scienze, Università degli Studi della Basilicata, Viale dell'Ateneo Lucano, 10, Potenza, 85100, Italy

^dCNR NANOTEC – Istituto di Nanotecnologia – c/o Dipartimento di Chimica, Università degli Studi di Bari “Aldo Moro”, 70126 Bari, Italy.

^eDipartimento di Chimica, Università degli Studi di Bari “Aldo Moro”, 70126 Bari, Italy.

^fDipartimento di Chimica e Biologia Adolfo Zambelli, Università di Salerno, Via Giovanni Paolo II, I-84084 Fisciano (SA), Italy

^gMaterials Characterization Facility, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

^hDipartimento di Chimica e Biologia Adolfo Zambelli, Università di Salerno, Via Giovanni Paolo II, I-84084 Fisciano (SA), Italy

Corresponding Authors

Lorenzo Malavasi, email: lorenzo.malavasi@unipv.it; Francesco Ambrosio, email: francesco.ambrosio@unibas.it

ABSTRACT

Photocatalytic nitrogen fixation (PNF) is a promising route for sustainable ammonia synthesis under ambient conditions. We report a simple, scalable synthesis of BiOBr/g-C₃N₄ heterojunctions across the full compositional range and evaluate their performance under simulated solar light. The optimal composite, containing 10 wt% BiOBr, achieved an ammonia evolution rate of $\sim 20 \mu\text{mol g}^{-1} \text{h}^{-1}$ —seven times higher than pristine g-C₃N₄—while maintaining structural and morphological stability over multiple cycles. Time-resolved spectroscopy revealed prolonged carrier lifetimes, confirming efficient charge separation and DFT calculations identified favorable band alignment and surface polaron formation as the origin of the enhanced activity. The results highlight an effective synergistic effect between BiOBr and g-C₃N₄ and provide mechanistic insight for designing scalable photocatalysts for green ammonia production.

1. Introduction

Sustainable ammonia (NH_3) production is a pressing goal for climate and energy security because ammonia is the backbone of nitrogen fertilizers and is also emerging as a potential carbon-free energy carrier.^[1–3] However, conventional ammonia synthesis via the Haber–Bosch process consumes tremendous fossil energy and emits significant CO_2 .^[4] This motivates the development of green ammonia production methods such as electrochemical synthesis which could be considered a sustainable alternative only if renewable energy is used.^[5] On the other hand, photocatalytic nitrogen fixation (PNF), which uses solar energy to drive the reduction of N_2 to NH_3 under ambient conditions, is an attractive sustainable approach.^[6–8] By harvesting sunlight to split water and activate N_2 , photocatalysis could drastically reduce the carbon footprint and energy intensity of ammonia synthesis, aligning with climate mitigation and renewable energy integration targets.

Among various photocatalysts explored for N_2 reduction, bismuth oxybromide (BiOBr) has gained attention as a visible-light-responsive semiconductor. BiOBr features a layered matlockite structure composed of $[\text{Bi}_2\text{O}_2]^{2+}$ slabs interleaved with bromide anions. This layered architecture gives BiOBr a band gap of about 2.7–2.8 eV that enables absorption of visible light.^[9–12] Moreover, the internal polarization between the bismuth-oxide layers and halide layers can induce built-in electric fields that promote charge separation.^[13] Thanks to these properties, pristine BiOBr can efficiently harvest visible photons and has shown activity in photocatalytic oxidation and reduction reactions with most of the application related to the degradation of organic pollutants under solar irradiation.^[14–16] Nonetheless, BiOBr alone still suffers from intrinsic limitations such as the rapid recombination of photogenerated electron–hole pairs in BiOBr leading to low quantum efficiencies.^[17] These drawbacks hinder its practical performance and motivate strategies to improve its photocatalytic efficiency.

To overcome the above limitations, recent studies have focused on engineering the electronic structure and interfaces of BiOBr by constructing heterojunctions with other semiconductors or conductive materials.^[14,15,17] Such well-known strategy in the field of photocatalysis has proven particularly effective for enhancing visible-light activity of BiOBr-based systems. Chang et al. reported one of the early successes by coupling BiOBr with graphitic carbon nitride (g-C₃N₄) into 3D hierarchical heterostructures for Rhodamine B degradation, demonstrating an improved charge separation under visible light due to the formation of the heterojunction.^[18] On this line, several other BiOBr-based systems have been then investigated by coupling BiOBr with graphene, α -Bi₂O₃, MoS₂, and polyaniline (PANI), among others.^[19–21] All these heterojunction have been tested for the degradation of dyes showing enhanced photodegradation rates with respect to pristine BiOBr.

Building on its general photocatalytic promise, BiOBr has more recently been investigated for the challenging reaction of N₂ fixation under mild conditions. In 2016, Li et al. first demonstrated that bismuth oxyhalides such as BiOCl can drive the reduction of N₂ to NH₃ under illumination sparking interest in BiOBr for green ammonia synthesis.^[22] According to this early study, BiOBr offers a favorable band structure for this reaction: its conduction band is sufficiently negative to reduce N₂ to NH₃ (thermodynamically), while the valence band can oxidize water to supply protons.^[22] However, BiOBr alone shows only modest nitrogen photofixation activity since N₂ molecules adsorb weakly on BiOBr surfaces, leading to inefficient N≡N activation and low NH₃ yields.^[23] It is well known, in fact, that nitrogen absorption requires the presence of vacancy defects in the form, for example, of nitrogen or oxygen vacancies.^[6,7,24] Recognizing these issues, researchers have turned to surface and interface engineering of BiOBr to improve N₂ reduction efficiency. Oxygen vacancies and surface defect engineering have been employed to strengthen N₂ chemisorption on BiOBr, while cocatalysts (such as noble metals or transition metal sites) have been added to activate N₂ at the surface.^[23] In addition, BiOBr-based heterojunctions have been designed to facilitate charge separation and provide energetically favorable pathways for photocatalytic N₂ conversion to ammonia.^[8,25,26] Zhao et al.

(2022) reported that constructing Z-scheme heterojunctions with BiOBr can greatly improve nitrogen photofixation. For example, a direct Z-scheme BiOBr/Bi₄O₅Br₂ catalyst showed superior NH₃ yields compared to pure BiOBr, due to more efficient charge carrier separation and retention of strong redox power in the Z-scheme system.^[27] Such heterojunctions mitigate the electron–hole recombination losses and ensure that enough energetic electrons reach the catalyst surface to activate N₂ molecules. Among the potential semiconductors to be coupled to BiOBr graphitic carbon nitride, g-C₃N₄, has been considered due to its good visible light absorption, high stability, and ease of preparation. Recently, Gao et al. constructed a tubular g-C₃N₄/BiOBr heterojunction that achieved an enhanced ammonia production rate with respect to pristine materials thanks to the close interaction between BiOBr nanospheres grown on the inner and outer surfaces of hollow g-C₃N₄ nanotubes.^[28] Such architecture, while efficient in the photocatalytic conversion of nitrogen to ammonia, requires however complex synthetic steps which hinder their scalability potential.^[29] Despite these encouraging developments, further improvements in BiOBr-based photocatalysts are needed to meet the demands of efficient green ammonia production.

To further explore the potential of BiOBr-based heterojunctions for the photocatalytic N₂ reduction reaction and try to elucidate the reaction mechanism, we afforded the investigation of the BiOBr/g-C₃N₄ (g-CN) nanosheets system by exploring the full compositional range between the two semiconductors. Thanks to a combined experimental and computational modelling work we uncover how interfacial charge dynamics, band alignment, and surface reactivity govern the observed performance trends. Our findings reveal an optimal composition that maximizes ammonia production while minimizing BiOBr content, offering new insight into the design principles for efficient and sustainable photocatalysts.

2. Results and Discussion

The BiOBr/g-CN nanosheets system has been synthesized according to the experimental procedure reported in the Supporting Information (SI) which is schematically represented in Figure 1. Weight ratios between BiOBr and g-CN investigated are (wt% of BiOBr) 100, 90, 75, 60, 45, 30, 15, 10, and 0. The procedure adopted here to obtain the BiOBr/g-CN nanosheets system is simple and easily scalable and make use of cheap precursors for the preparation of g-CN.

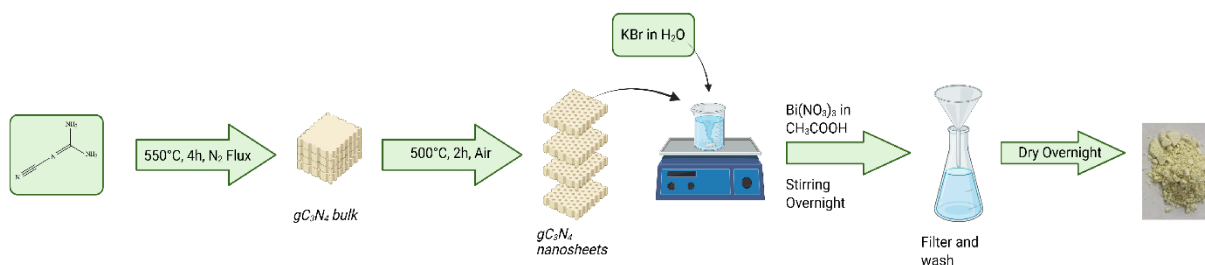


Figure 1. Schematic illustration of the synthetic procedure to obtain the BiOBr/g-CN samples.

The X-ray diffraction (XRD) patterns of the different compositions are reported in Figure 2a. Figure 2b and 2c report the patterns of pristine materials, namely BiOBr (against the calculated diffraction from reference crystal structure) and g-CN, respectively.

From Figure 2a it can be seen the prominent contribution of the BiOBr which has a higher scattering density with respect to g-CN and dominate the composite patterns for concentration above 30wt%. BiOBr (see Figure 2b) shows the typical tetragonal crystal structure (space group $P4/nmm$) with lattice parameters of about $a=b= 3.916$ and $c= 8.110$ Å. The diffraction pattern of pure g- C_3N_4 nanosheets (Figure 2c) presents the typical broad peaks around 13° and 28° corresponding to the (100) and (002) reflections.^[25]

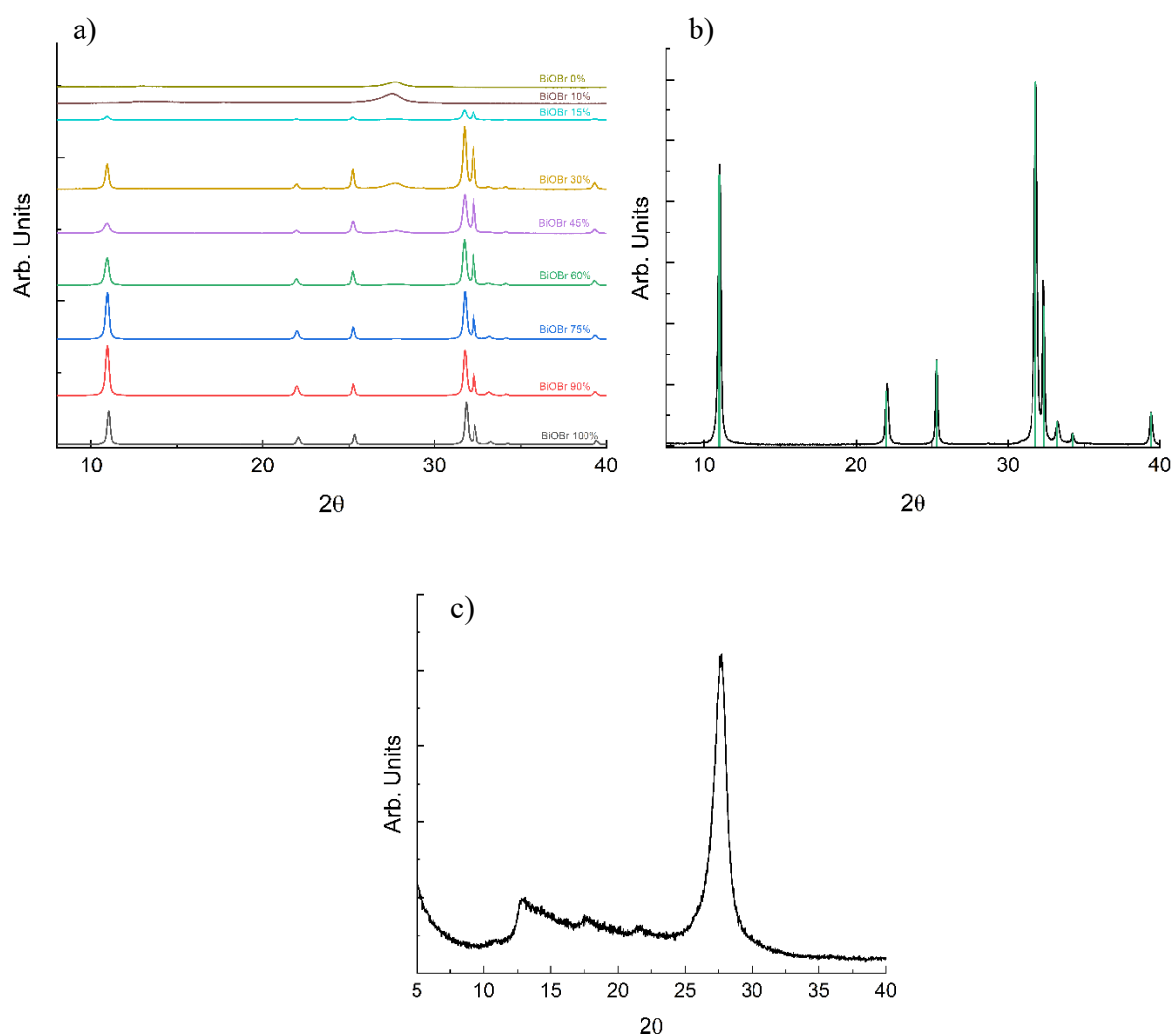


Figure 2. a) XRD patterns of BiOBr/gCN as a function of BiOBr wt%; b) BiOBr XRD pattern against calculated pattern; c) g-CN diffraction pattern.

The study of the morphological properties of the samples has been carried out by scanning electron microscopy (SEM) and the results are reported in Figure S1. In particular, we reported the images of the systems showing the best performance in the ammonia photogeneration (see later in the text), namely those containing 10wt% of BiOBr with respect to g-CN. A peculiar flower-like morphology has been observed for the BiOBr (Figure S1a) while this aspect is less evident in the BiOBr/g-CN system. A representative elemental map for BiOBr 10wt% over g-CN is as well reported in the SI (Figure S1b and c) demonstrating a homogeneous distribution of the bismuth oxybromide over the g-CN.

UV-Vis absorption spectra and the corresponding Tauc plots for BiOBr/g-CN system are reported in Figure 3. The indirect band gap of pure BiOBr is around 2.78 eV and that of pure g-CN

around 2.70 eV, in agreement with previous experimental and computational studies. Composites between the two samples show slight variations of the band gap energy with intermediate values between the pristine samples. The presence of g-CN tends to extend the absorption in the visible region through an extend tail characteristic of samples with low-crystallinity as in the case of the amorphous-like structure of g-CN.^[14,30,31]

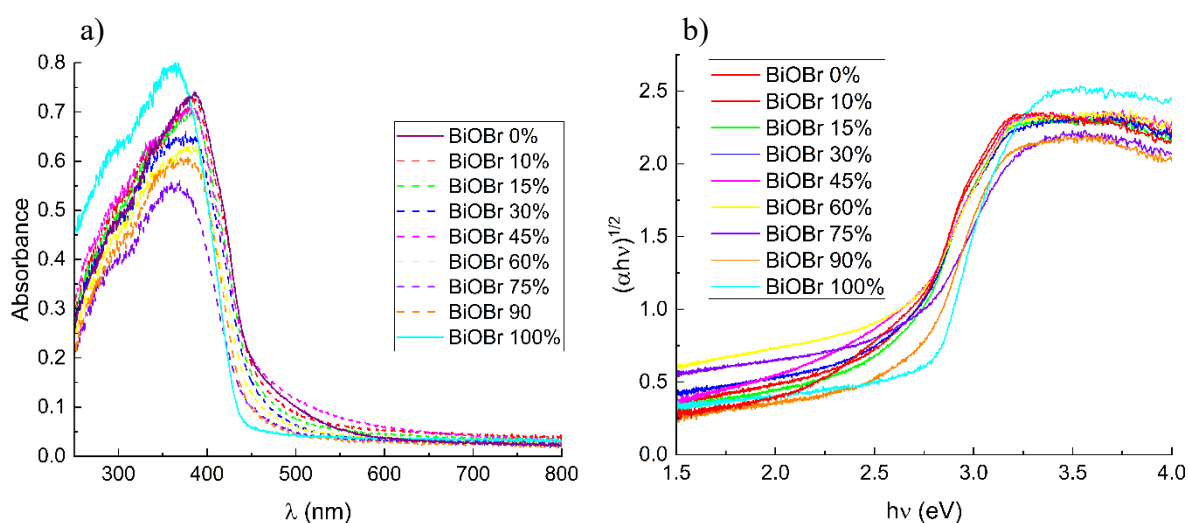


Figure 3. a) Absorption spectra and b) Tauc plots for samples of the BiOBr/g-CN system.

Figure 4 reports the results in terms of ammonia evolution rates, expressed as $\mu\text{mol g}^{-1}\text{h}^{-1}$, obtained by photocatalytic experiments under simulated solar light. Experimental details are provided in the SI for both the photocatalytic experiments and the ammonia determination technique which has been done making use of an ammonia ion selective electrode (ISE), which guarantees accurate detection over colorimetric methods.^[25,26,29]

The trend of ammonia evolution rate steeply increases from pure g-CN (about $3 \mu\text{mol g}^{-1}\text{h}^{-1}$) to the composite including BiOBr 10 wt%/g-CN 90 wt% reaching the highest value of about $20 \mu\text{mol g}^{-1}\text{h}^{-1}$. Such value then progressively reduced by increasing the BiOBr amount up to 75wt% and the increases again showing an effective ammonia photogeneration also for pure BiOBr with a rate of $\sim 8 \mu\text{mol g}^{-1}\text{h}^{-1}$.

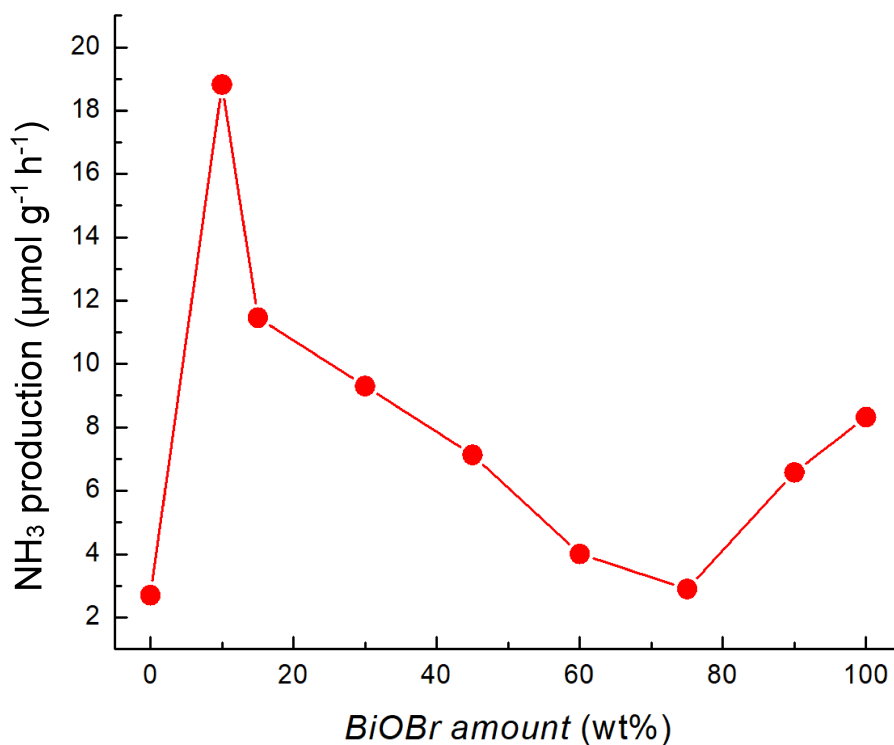


Figure 4. Ammonia productions as a function of BiOBr wt% in the composites. ($n=3$, simulated solar light, 500 W m^{-2}).

The data reported in Figure 4 demonstrate, first of all, that both pure materials have a certain degree of activity in the nitrogen reduction reaction with BiOBr alone performing better than g-CN. The creation of the heterojunction promotes the photocatalytic nitrogen reduction to ammonia, in particular for the BiOBr 10 wt%/g-CN 90 wt% composition, namely that presenting the lowest amount of bismuth oxybromide among those investigated which is a good result in term of sustainability of the system presented. The stability of the ammonia production has been tested on the top performing composite for four successive cycles as reported in Figure S2. Post-catalysis XRD and SEM data are shown in Figure S3, indicating the stability of the system both from a structural and morphological point of view.

The best-performing composition, together with pure BiOBr and g-CN, have been investigated by X-ray Photoelectron Spectroscopy (XPS). Figure S4 shows the wide scan spectra

collected on the three samples, while Figure S5 shows the high-resolution spectra. By looking at the high-resolution spectra, it can be seen that the nanoexfoliated g-CN sample is characterized by intense N 1s and C 1s signals, with main peaks centered at (398.8 ± 0.2) eV and (288.3 ± 0.2) eV, respectively, associated with pyridinic N and with the carbons in the N–C=N moieties, in line with reports on related systems.^[32,33] The BiOBr sample shows intense Bi 4f peaks, with the Bi 4f_{7/2} component centered at (159.4 ± 0.2) eV, as well as Br 3d and O 1s signals, with peaks centered respectively at binding energies of (68.5 ± 0.2) eV and (529.9 ± 0.2) eV. The observed positions are in line with literature reports on the material.^[34] The BiOBr 10 wt%/g-CN 90 wt% sample displays signals of both BiOBr and graphitic carbon nitride. While the signals from g-CN do not show significant variations with respect to the pure sample, a shift of -0.3 eV was observed on Bi- and Br-related peaks from BiOBr, suggesting that the interaction with g-CN might have induced some electronic rearrangements, with partial electron transfer to BiOBr. This should have induced a partial positive charge on g-CN, which should have resulted in a shift of the XPS signals to higher binding energy. The large excess of g-CN in the optimized system might have hidden this phenomenon.

In order to shed light on the different performances of the samples we first of all monitored the emission of the two pure materials and the heterojunction with the best performances (BiOBr 10 wt%/g-CN 90 wt%).

As we can notice from Figure 5 the emission of g-CN is centered at 480 nm, while the emission of BiOBr is at 465 nm. The emission of the heterojunction is slightly blue shifted compared to the carbon nitride due to the fact that the emission is dominated by the radiative recombination in the graphitic carbon nitride with only a slight contribution from BiOBr.

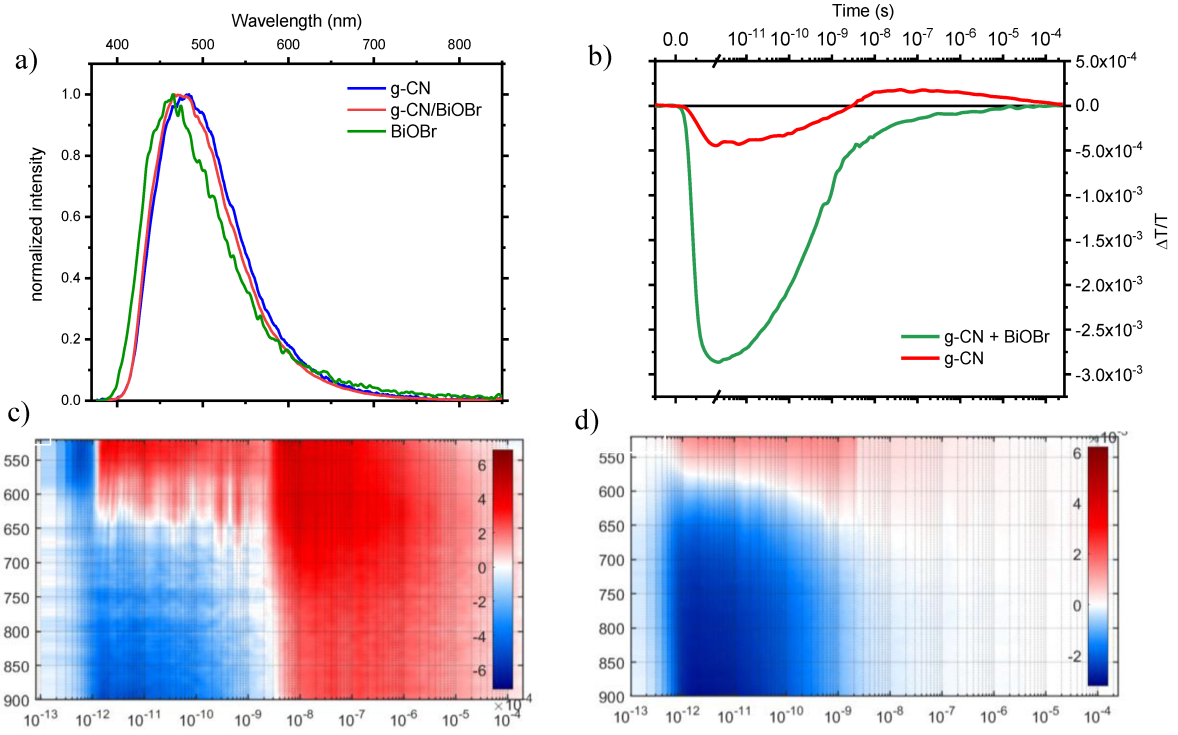


Figure 5. a) PL spectra upon 355nm excitation of g-CN (blue), BiOBr (green) and BiOBr 10 wt%/g-CN 90 wt%. b) Photoinduced absorption dynamics collected between 800 and 900 nm in a time range up hundreds of μ s. 2D map representing the transient absorption measurements taken in a wavelength range between 520 and 900 nm and in a time range up to 250 μ s on c) g-CN and d) BiOBr 10 wt%/g-CN 90 wt%.

We then monitor the carrier dynamics after light absorption in the different materials using transient absorption spectroscopy measurements. As we can see in Figure 5c and 5d, at early time (< 1 ns), the g-CN and heterojunction share similar spectra. Both show a broad photobleach signal (red shades) between 520 and 575/675 nm which correspond to band edge states filled upon excitation. The difference in width of this signal, despite a very similar position of the absorption edge, can be related to a different population of defect and distortion, as corroborated by the higher shoulder below the band edge in the case of g-CN compared to the sharper edge of the 10% BiOBr (Fig. 5a). At longer wavelength it is possible to see a broad and negative photoinduced signal up to 900 nm (blue

shades). This negative signal is related to charge carrier promotion after the excitation. At longer time ($> 1\text{ ns}$) we can notice a clear difference between the two samples. For g-CN sample the signal turn to positive due to trapping of carriers within the bandgap from which they likely recombine non radiatively. On the other hand, the photoinduced absorption (PIA) signal in the presence of BiOBr last up to tens of μs making the carriers available for a longer time for the charge transfer from the photocatalyst to the nitrogen molecule. In the case of pure BiOBr (Figure S6) can notice a really broad positive signal due to a high degree of defectivity of this material. It's worth noting that this signal goes to 0 in 20/25 μs , while in the case of CN and the BiOBr/g-CN heterojunction it lasted to at least 100 μs . Overall, these results confirm, on one side, the formation of the heterojunction, and, more importantly, its effective role in making charge carrier dynamics available for the nitrogen reduction reaction.

In order to get further insight into the photoelectrochemical processes at the root of the observed NH_3 production, we here determine the band alignment for the materials under study, via advanced electronic-structure calculations based on piece-wise linear hybrid density functional theory (DFT, cf. SI for computational details). The data presented for g- C_3N_4 are taken from previous studies of some of us, Ref. 32, while we here instead focus on BiOBr: first, we determine the room-temperature fundamental band gap of the oxyhalide which is found to be 3.07 eV, when including the effect of thermal motion at room temperature and spin-orbit coupling (cf. SI for details of the calculations).^[35] Considering that exciton binding energies up to 0.1 eV have been measured for BiOBr, the calculated value is in very good accord with the experiment.^[36,37] We also note that the band gap reported here is 0.27 eV larger than a previous theoretical estimate, which, however, were performed employing a density functional, HSE06, that tends to slightly underestimate band gaps of Bi-based semiconductors.^[38–40]

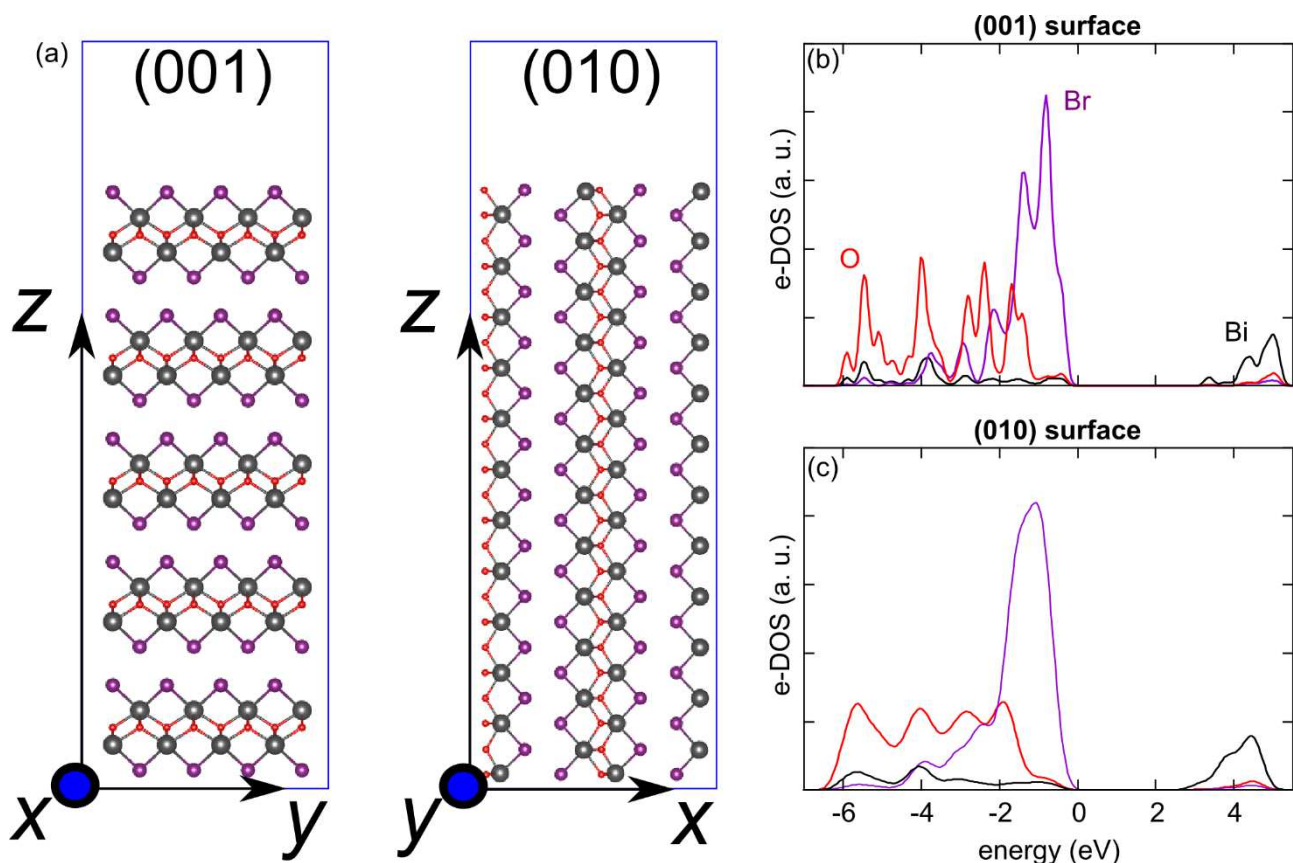


Figure 6. a) Stick&Ball representation of the atomistic models employed to simulate the (010) and the (001) surfaces of BiOX materials. O is in red, X=Br, I in purple, and Bi in grey. Electronic density of states (e-DOS) calculated for the slab models of the (001) and (010) surfaces (b and c panels, respectively).

To study the alignment of the energy levels for materials under study, we consider two different surface terminations for the band alignment of BiOBr: the bulk-like (001) and the (010) surfaces [cf. Figure 6a, the former being approx. four times more stable than the latter (cf. SI)]. Analysis of the electronic density of states (e-DOS), cf. Figure 6b-c and Figure SF1, reveals that indeed the (001) surface possess band edges similar to those of the bulk material: the valence band is mainly constituted by Br 4p states with minor but significant contributions from O 2p and Bi 6s states, while the conduction band has a strong Bi 6p character. The e-DOS for the (010) surface features augmented contributions of Bi states to the band edges due to undercoordinated surface Bi atoms, which suggests an increased reactivity for this system.

For the (001) surface, our DFT modelling (cf. SI) places the valence band maximum (VBM) and the conduction band minimum (CBM) 8.07 and 5.00 eV below the vacuum level, respectively, as illustrated in Figure 7a. This, in conjunction with the corresponding energy levels for g-C₃N₄ at 6.00 and 3.00 eV vs. vacuum, correspond to a type II alignment for the composite formed by the two semiconductors. This is indeed favorable for charge separation across the interface as holes are expected to migrate towards g-C₃N₄ while electrons are transferred to BiOBr. However, we note that the N₂/NH₃ redox level is found to lie 0.23 eV above the CBM of BiOBr, thus implying a barrier for the reduction reaction which is not desirable for a swift completion of N₂ fixation. At variance with this, when considering the (010) surface of BiOBr, cf. Figure 7b, the band edges of the oxybromide are found to be pushed closer to the vacuum level, as we calculate values of VBM and CBM at 6.51 and 3.44 eV, respectively. Therefore, a suitable band alignment with g-C₃N₄ is preserved but now with a downhill pathway for N₂ reduction: considering the inverse exponential dependence of the reaction rate on the energy level difference, this alignment is even more favorable than that of bare g-C₃N₄.^[41] This result is consistent with the observed better performance of BiOBr with respect to g-C₃N₄, when tested individually. Furthermore, the sizably different alignments calculated for the (001) and (010) suggests a possible role of the morphology in the composition-dependent performance of the g-C₃N₄/BiOBr heterojunctions.

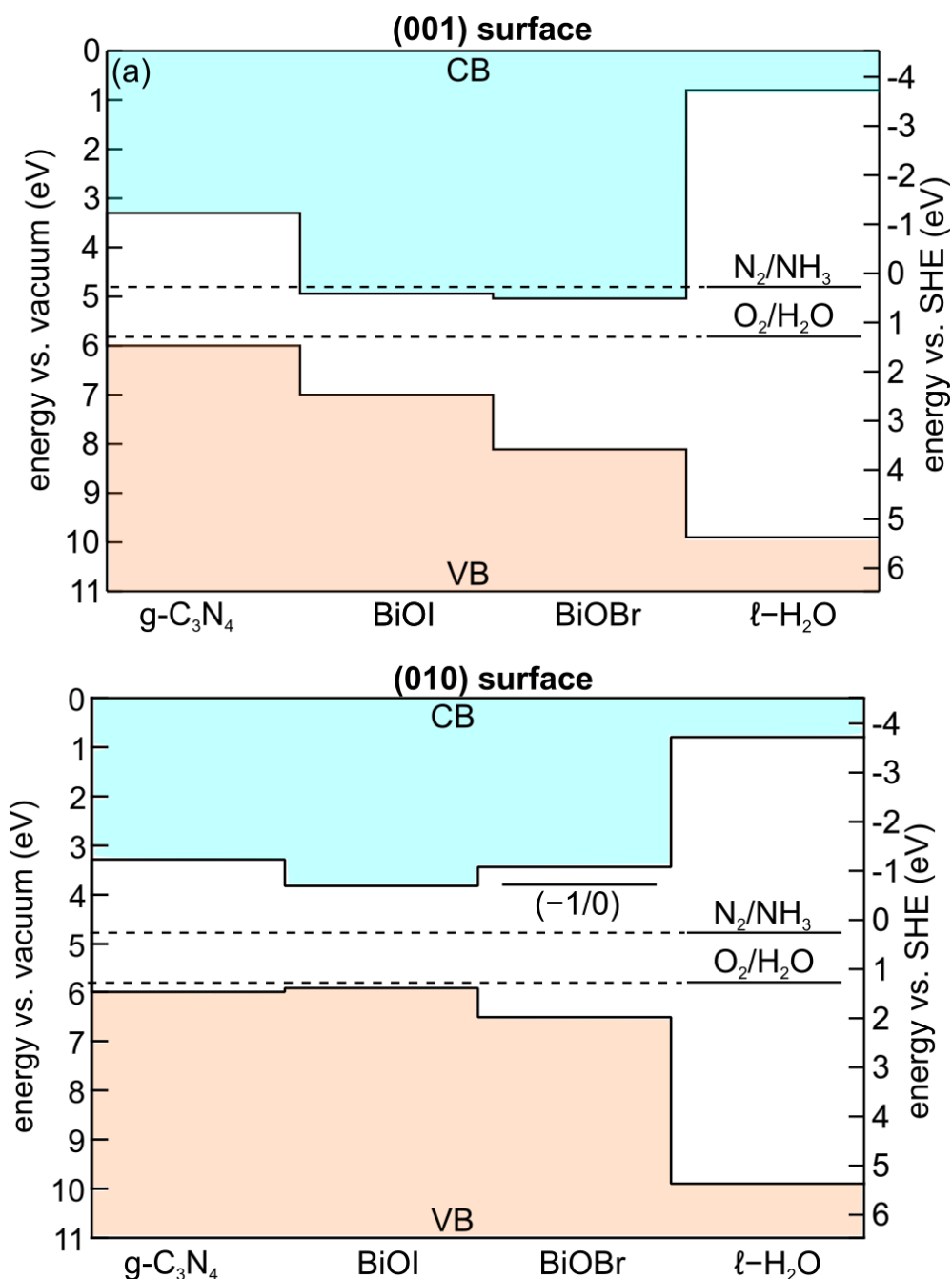


Figure 7. Valence band (VB) and conduction band (CB) edges of g-C₃N₄ and BiOX aligned with the band edges of liquid water and with the N₂/NH₃ and O₂/H₂O redox levels through the vacuum level. We also report the energies referred to a computational standard hydrogen electron developed in Refs. 39 and 40.^[42,43] Alignment is performed considering the (001) and the (010) surfaces of BiOX semiconductors, see panel a) and b) respectively. The (-1/0) charge transition level for the electron at the (010) surface of BiOX. All values are given in eV.

We note that in a previous study on g-C₃N₄/Cs₃Bi₂Br₉ composites, it was suggested that a similar trend in the photocatalytic production of H₂ could be ascribed to the presence of small electron polarons in the layered perovskite.^[44] This in turn would be more easily trapped in the bulk region,

when larger loads of the materials are employed. However, in the present case, it has been demonstrated in Ref. 42 that electron polarons are unstable in bulk BiOBr, thus ruling out an analogous explanation of the observed phenomenon.^[45] Nevertheless, it has been shown, for different photocatalysts, that charge localization at the surface may be key in boosting the conversion efficiency within unconventional reaction mechanisms. For this reason, we here verify the occurrence of electron polarons at the (001) and (010) surfaces, by calculating the polaronic energy levels (cf. SI). For the (001) surface, we do not find any local distortion leading to surface charge localization: the electron remains delocalized, as in the bulk material, cf. Figure 8a, a result consistent with the passivated nature of the surface.^[46] In stark contrast, we observe small polaron formation at the (010) surface, cf. Figure 8b: electron localization is found to occur on an undercoordinated surface Bi upon local distortion of Bi-Br and Bi-O bonds. In particular, a single Bi atom is shifted upwards with respect to the slab plane, a phenomenon which causes an elongation of its bonds of ~ 0.15 Å, with respect to the neutral system. The polaronic state, found at 0.4 eV below the vacuum level, cf. Figure 8b and SI, may serve as a hotspot for the reduction reaction, in line with previous results on other semiconductors, thus further supporting the reactivity of the (010) surface.^[47,48]

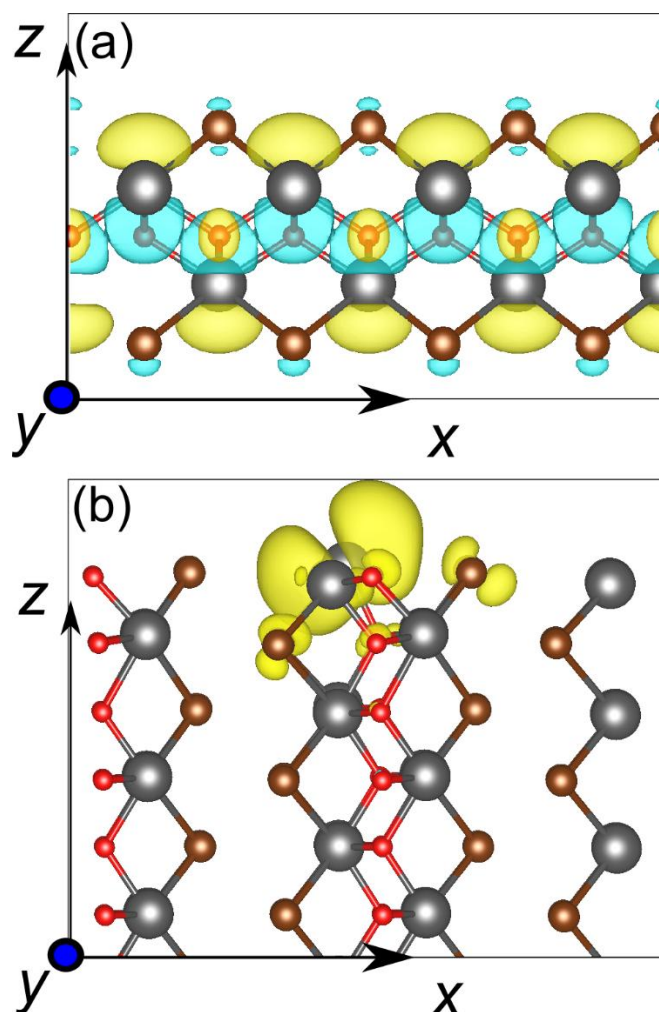


Figure 8. Isodensity representation of a) the highest occupied molecular orbital for the negatively charged (001) slab model and b) the spin density associated with the small polaron for the negatively charged (010) slab model. Bi atoms in grey, O atoms in red, Br in bronze.

Finally, since halide substitution/alloying has been suggested to enhance the efficiency of metal halide perovskites and related materials, we here also consider, for comparison, the oxyiodide with analogous structure, BiOI, for which we calculate a reduced fundamental band gap of 2.06 eV.^[49] For the (001) surface, the VBM is found at 7.00 eV while the CBM at 4.94 below the vacuum level, cf. Figure 7a. Therefore, the main difference with respect to BiOBr is due to the shift of the VBM of 1.07 eV, while the CBM, which is mainly composed by Bi states, is almost unaffected. The calculated alignment again implies a small energy barrier for the electron transfer reactions associated with N_2 fixation. At variance with this, when considering the (010), as depicted in Figure 7b, we retrieve a desirable alignment with the N_2/NH_3 redox level. However, the electron polaron is found to be

unstable at the (010) surface of BiO, a consequence of the lower energy level of the CBM for the iodide, an instance observed also in other cases, e.g. tin halide perovskites.^[50] Furthermore, in this case, the alignment with g-C₃N₄ becomes type I, with both holes and electrons being more stable in the oxyhalide, thus limiting the efficiency of such a composite. Overall, while Br/I substitution might not be practical in this case, alloying could be a strategy to pursue in order to have at the same a suitable band gap and a favorable alignment of energy levels.

In conclusion, the results of computational modelling suggest that the enhanced reactivity of the composite is promoted by a suitable alignment of energy levels. Furthermore, the composition-dependent trend in ammonia production which features optimal values for low loading of BiOBr can be interpreted with the varying morphology of the system at different weight%. In fact, we can suppose that the relative exposure of the more reactive (010) surface - in virtue of its better band alignment and the occurrence of surface polarons - and the bulk-like and more inert (001) surface may vary with composition. In particular, as the (001) surface is sensitively more stable than the (010), nanoparticles are likely to grow preferentially along the former direction. This in turn may lead to large domains of poorly reactive (001) surfaces with systems with a larger percentage of composite. We also note that another possible bottleneck for charge mobility is given by hole polaron, which have been predicted in the bulk.^[50] Their reduced mobility, if compared with free charges, might also hinder charge transport across g-C₃N₄/BiOX interfaces. Nevertheless, further studies are needed understand the origin of the promising NH₃ production here documented, also in connection with the reaction mechanism.

3. Conclusions

In this study, we have systematically investigated the photocatalytic nitrogen fixation performance of BiOBr/g-C₃N₄ heterojunctions across the full compositional range, prepared via a facile, low-cost, and scalable synthetic route. The results demonstrate that coupling these two semiconductors leads to a marked improvement in ammonia production rates under simulated solar light, with the optimal performance achieved for a composition containing 10 wt% of BiOBr. This composite exhibited an ammonia evolution rate of $\sim 20 \mu\text{mol g}^{-1} \text{h}^{-1}$ - nearly seven times higher than pristine g-C₃N₄ and more than twice that of pure BiOBr - while maintaining excellent structural and morphological stability over multiple reaction cycles.

The enhanced activity of the heterojunction can be attributed to improved charge separation and transfer efficiency, as evidenced by photoluminescence quenching, extended carrier lifetimes observed in transient absorption spectroscopy, and band alignment analysis. Density functional theory (DFT) calculations provided deeper mechanistic insight, revealing that the superior performance could be linked to the exposure of the less stable but more catalytically active BiOBr (010) surface. This surface features favorable energy level alignment with g-C₃N₄ for downhill electron transfer to N₂, as well as the formation of surface polarons that act as localized electron-rich sites for N₂ activation. In contrast, the more stable BiOBr (001) surface exhibits an energy barrier for nitrogen reduction, explaining the performance drop observed at higher BiOBr loadings where growth along the (001) direction dominates.

The observed synergy between g-C₃N₄ and BiOBr, especially at low BiOBr loading, offers a sustainable path forward by reducing reliance on heavy bismuth content while achieving high activity. Beyond the BiOBr/g-C₃N₄ system, the mechanistic framework established here—linking facet-dependent band energetics, charge carrier dynamics, and surface polaron formation to catalytic performance—can be extended to the rational design of other heterojunction-based photocatalysts. Ultimately, this work advances our understanding of nitrogen photofixation mechanisms and provides

a foundation for the development of efficient, scalable, and environmentally benign routes for solar-driven ammonia production.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5tc04124d>.

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SUPPLEMENTARY INFORMATION

Mechanistic Insight into the Nitrogen Photofixation

Reaction by BiOBr-based Heterojunctions

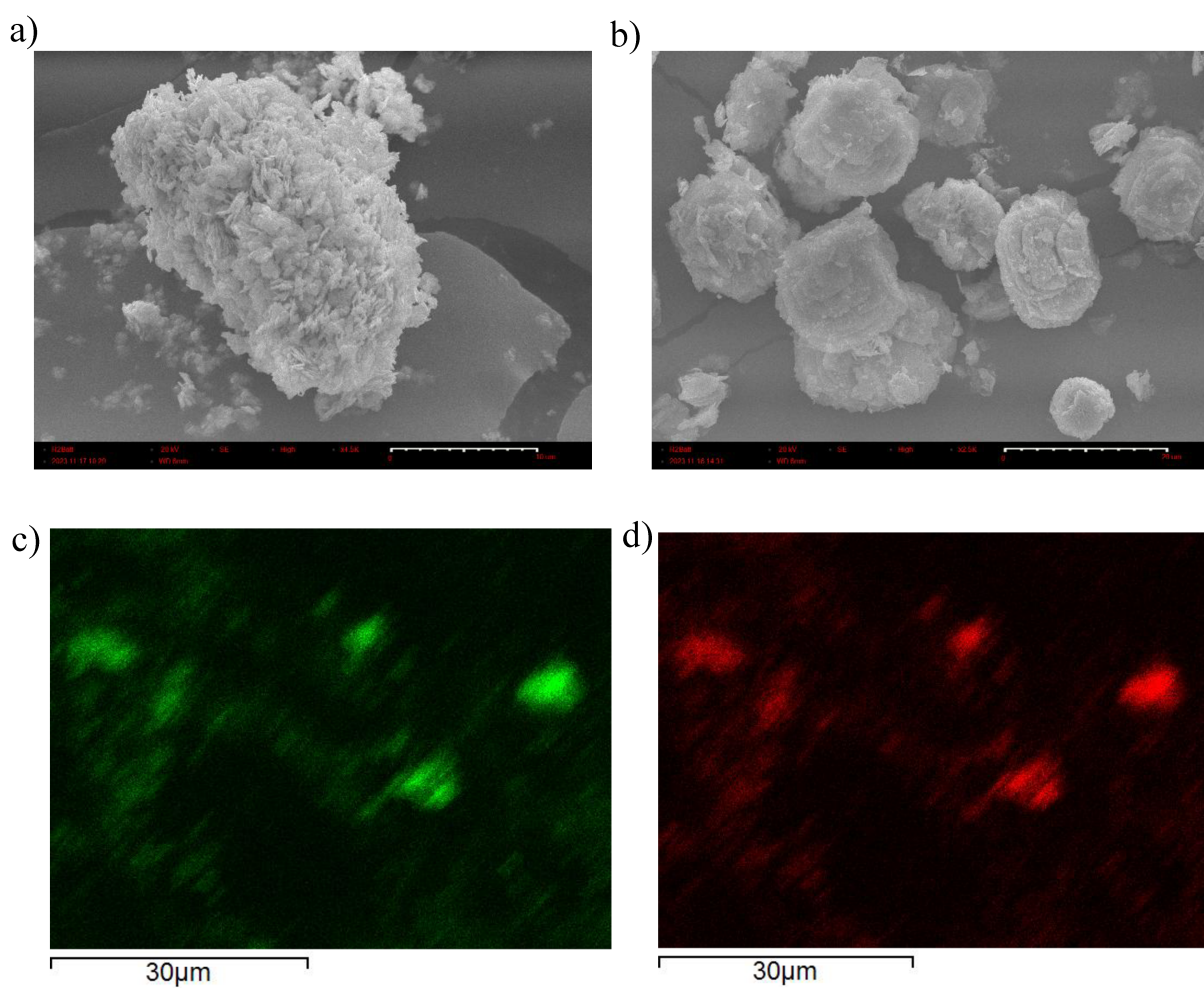


Figure S1. Representative SEM images of a) BiOBr; b) BiOBr10%/gCN 90% (best performing composite for ammonia photogeneration; c) Bi and d) Br elemental maps of BiOBr10%/gCN 90%.

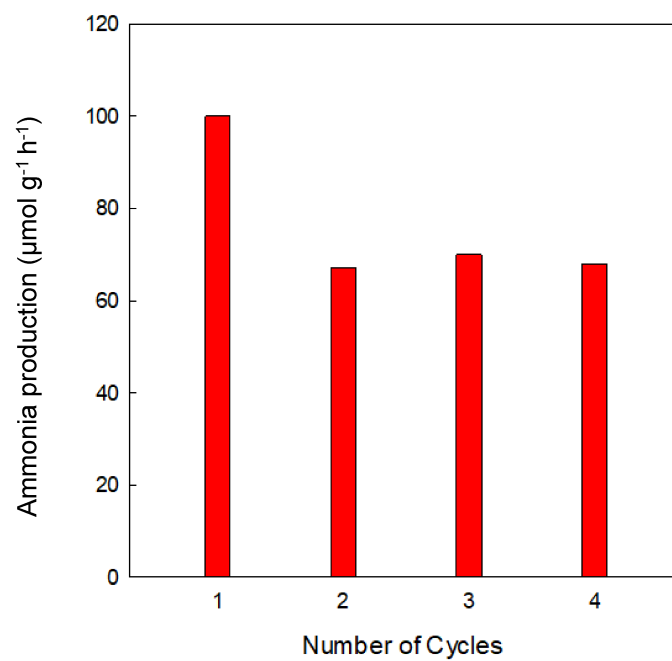


Figure S2. Trend over four cycles for the best performing composite, namely BiOBr 10 wt%/gCN 95 wt%.

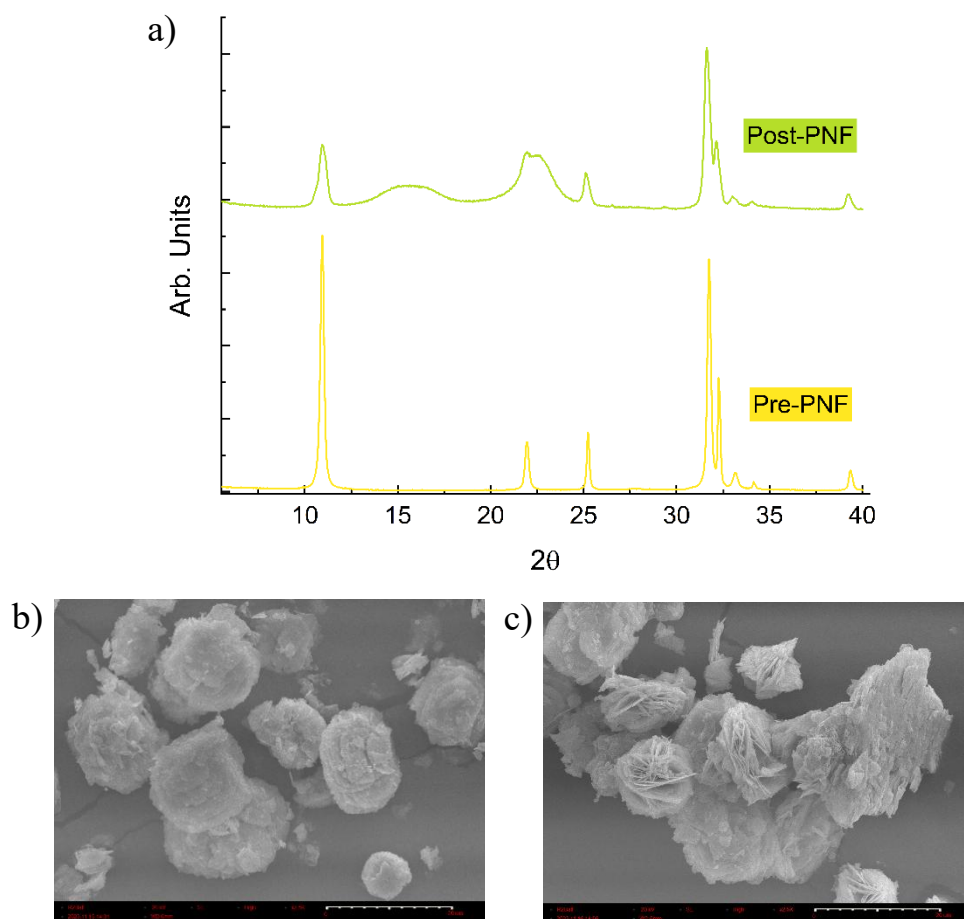


Figure S3. a) XRD of the BiOBr 10 wt%/gCN 90 wt% before and after the photocatalysis; b) and c) are illustrative images of BiOBr 10 wt%/gCN 90 wt% before and after the photocatalytic test.

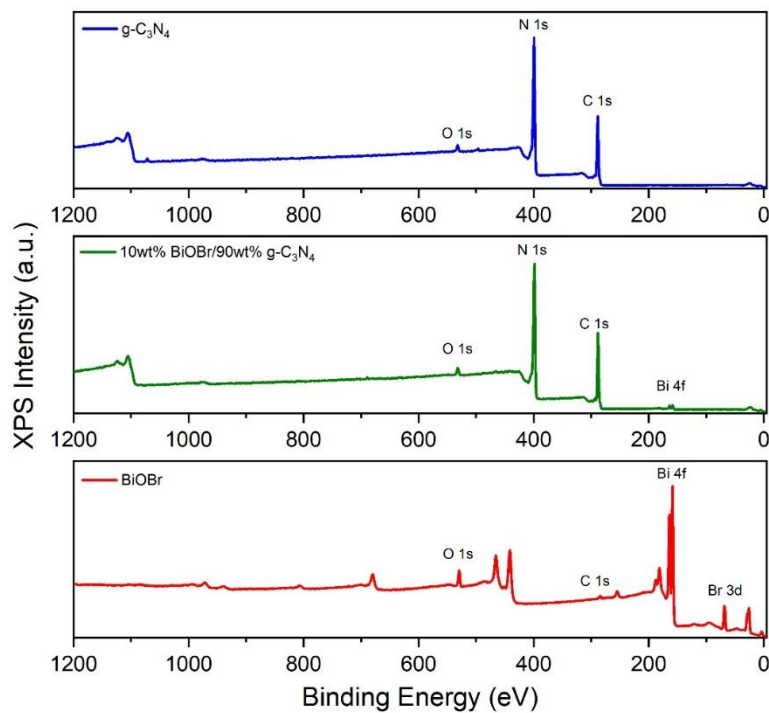


Figure S4. Comparison of the wide scans collected on the three analysed samples – from top to bottom: $g\text{-C}_3\text{N}_4$, BiOBr 10 wt%/gCN 90 wt%, and BiOBr.

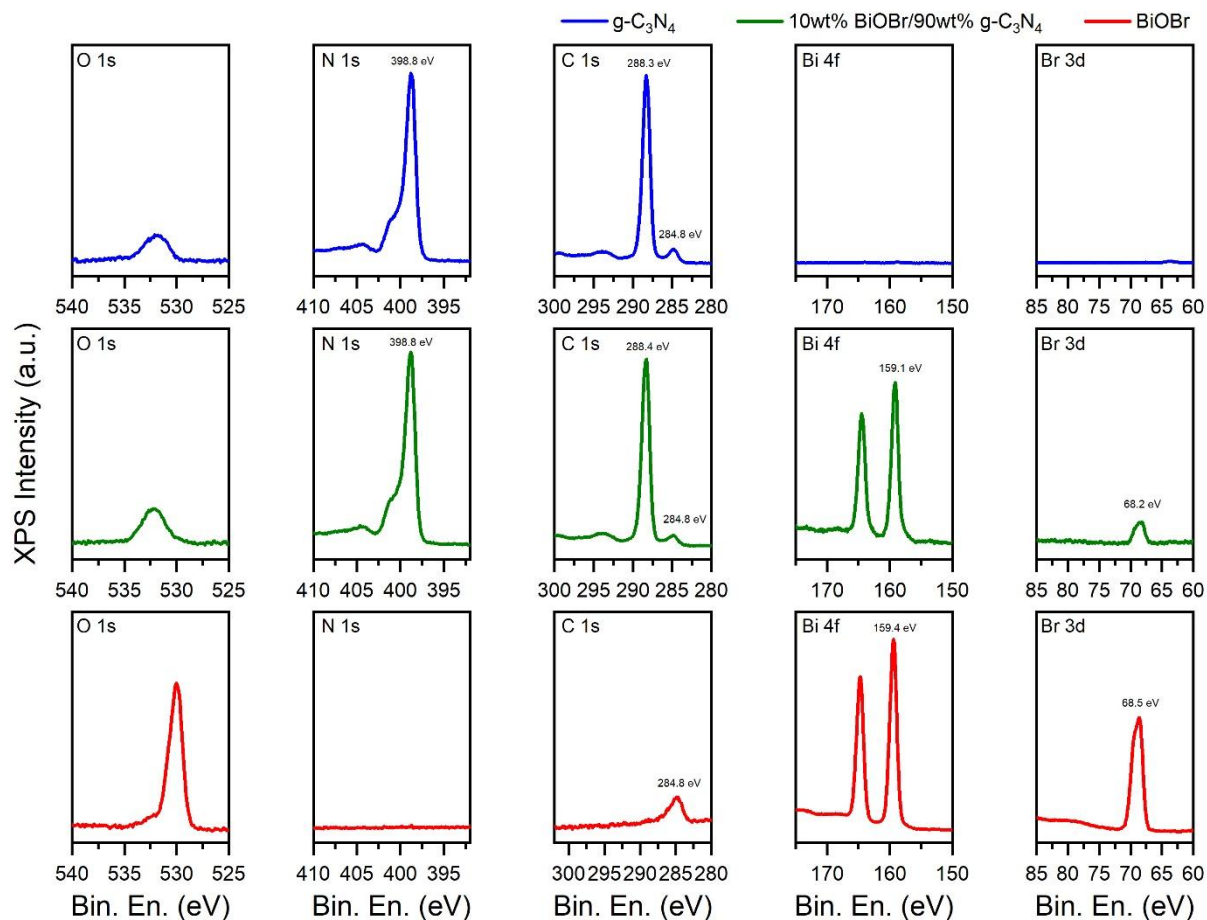


Figure S5. Comparison of the high-resolution spectra collected on the three analysed samples – from top to bottom: $g\text{-C}_3\text{N}_4$, BiOBr 10 wt%/gCN 90 wt%, and BiOBr.

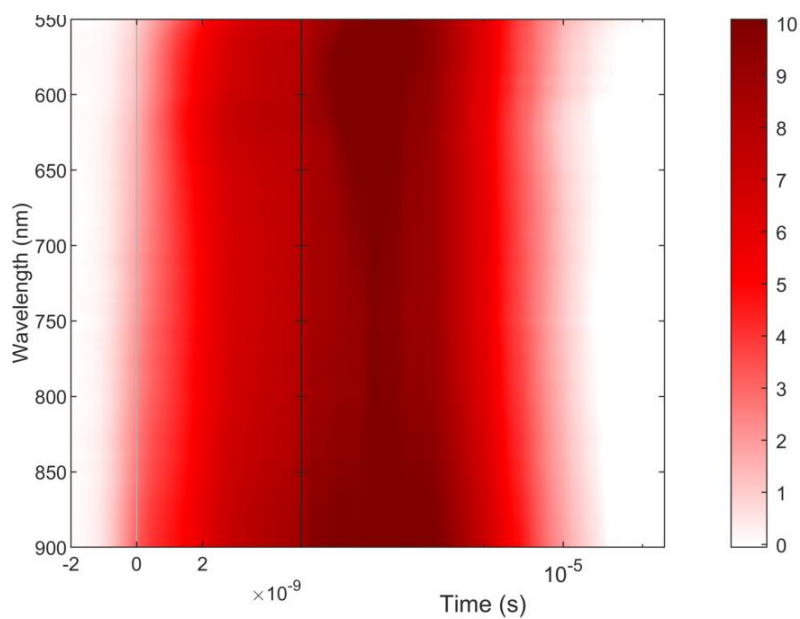


Figure S6. 2D map representing the transient absorption measurements taken on BiOBr sample, in a wavelength range between 550 and 900 nm and in a time range up to 25 μs

Experimental Section

Sample synthesis and characterization

g-C₃N₄ nanosheets have been synthesized starting from the bulk form (bulk g-C₃N₄).

Dicyandiamine DCD (NH₂C(=NH)NHCN, Aldrich, 99%) is polymerized under N₂ flux: the alumina boat containing densely packed DCD is positioned in a quartz tube, filled with nitrogen, and heated up in a tubular oven (4 °C min⁻¹) to the selected temperature of 550 °C, followed by an isothermal step 4 hours long and finally cooled to room temperature (6 °C min⁻¹).

To produce thermally exfoliated nanosheets, 1 gm of finely ground bulk g-C₃N₄ was placed in an alumina boat (20 mL), spread to cover homogenously the bottom, and heated (5 °C min⁻¹) in a tubular oven under air until the desired temperature was reached. The boat was left at the desired temperature for 2 h and then cooled (6 °C min⁻¹) until reaching room temperature.

The BiOBr/g-C₃N₄ nanosheets composites have been synthesized by wet co-precipitation: Bi(NO₃)₃ · 5 H₂O is dissolved in acetic acid (solution A) and then added to solution B (KBr dissolved in distilled, DI, water) in which is dispersed the right stoichiometric amount of g-C₃N₄ nanosheets for achieving the desired ratio. The obtained mixture is then left to stir for a night, and, after that, the composite is filtered, washed with DI water and ethanol, and left under the fume-hood to dry overnight. The composite series has been realized with the following BiOBr percentages: 100, 90, 75, 60, 45, 30, 15, 10, 0.

The crystal structure of the samples has been characterized by room temperature Cu-radiation XRD acquired with Bruker D2 diffractometer. DRS spectra were acquired in the wavelength range 300-800 nm directly on the powders by using a Jasco V-750 spectrophotometer, equipped with an integrating sphere (Jasco ISV-922). Microstructural characterization of the samples was made using a high-resolution scanning electron microscope (SEM, TESCAN Mira 3) operated at 25 kV.

Nitrogen Photofixation Experiments and Ammonia Determination

N₂ photofixation experiments were conducted in tridistilled water containing 10% (v/v) methanol (Aldrich, ≥99.9%) irradiated in a Pyrex glass container (250 mL capacity, 100 mL sample). Methanol plays the role of sacrificial agent, whose job is to minimize the recombination of electron and holes – by being oxidized faster than water – and maximize electron extraction. After addition of the catalyst (0.5 g L⁻¹), the sample suspension was deoxygenated by N₂ bubbling (45 min) to obtain a saturated solution and then irradiated under magnetic stirring for 3

hours maintaining the temperature at 15°C. Irradiation was performed under simulated solar light (1500 W Xenon lamp, 300-800 nm) using a Solar Box 1500e (CO.FO.ME.GRA S.r.l.) at 500 W/m².

The quantification was performed with ammonia ion selective electrode (ISE), which guarantees accurate detection over colorimetric methods (e.g. Nessler method) as previously assessed.^[1,2] The Thermo Scientific Orion Ammonia Ion Selective Electrode (ISE) was selected as it measures ammonia ions in aqueous solutions quickly, simply, economically, and accurately. It uses a hydrophobic gas-permeable membrane which separates the sample solution from the electrode filling solution. Water does not wet the membrane and does not penetrate the holes, whereas the dissolved ammonia in the sample solution diffuses through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. In any sample the partial pressure of ammonia is proportional to its concentration.

Daily freshly tri-distilled water, free of volatile amines that can positively interfere with the measurements, was used for all standards and samples. The pH of all standards and samples was adjusted above 11 with a strong base (10 N NaOH, ion strength < 1M), so that dissolved ammonia (NH₃(aq) and NH₄⁺) is converted to NH₃(aq): ionic species present in the standard and sample solutions cannot cross the membrane but can change the solubility of ammonia and/or form metal complexes. Basification removes most metals in the form of hydroxide complexes or precipitates.

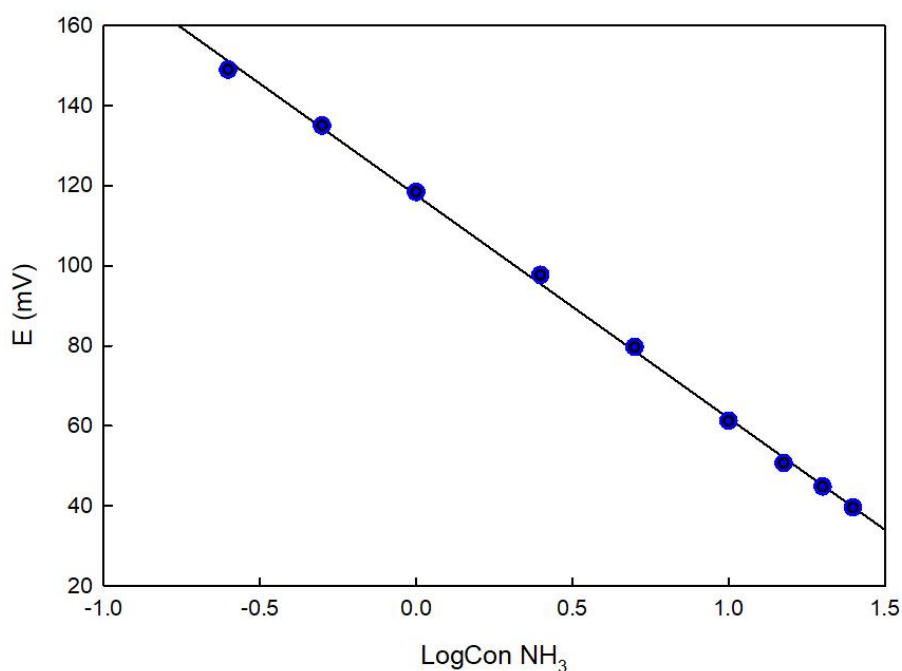


Figure S7. Mean calibration curve ($n=7$) for ammonia quantification (0.25 mg L⁻¹ ÷ 25 mg L⁻¹ as NH₃).

All measurements were performed in a beaker with minimized surface area/volume ratio, at a uniform and moderate rate, under controlled temperature. Since temperature changes can cause a change of the slope and potential, a piece of insulating material, e.g., ceramic or cardboard, was placed between the magnetic stirring plate and beaker to prevent measurement errors because of a heat transfer to the sample. In details, ISE was immersed in the solution (standard or sample, 1% v/v 10 N NaOH, 10% v/v MeOH) until a stable potential value (mV) was obtained. For the quantification, a calibration curve was constructed daily plotting the mV value recorded after 2 minutes equilibration time against the Log Concentration, to verify the slope (varying in the range $-54 \div -60$ mV). The ammonia concentration in the sample was further assessed by two standard additions. Figure S7 reports an example of mean calibration curve ($0.25 \text{ mg L}^{-1} \div 10 \text{ mg L}^{-1}$ as NH_3).

Optical Spectroscopic characterization

Transient absorption spectroscopy (TAS) measurements were performed in transmission mode on powder samples dispersed in DMF with a concentration of 5 mg/ml. A femtosecond laser (Light Conversion Pharos) generates pulses of 280 fs centered at 1030 nm. Focusing a part of this fundamental beam on a sapphire plate a broadband white light was generated, spanning from 520 to 900 nm, which was used as probe beam. At short delays (<3 ns), the pump beam was generated from the third harmonic of the fundamental providing a wavelength of 343nm. At long delays (>3 ns), we used a Q-switched Nd YVO4 laser (Innolas Picolo) to generate a 355nm pump beam electronically triggered to control the delay between pump and probe. Photoluminescence (PL) measurements were conducted by using the same pump used for fs-TAS measurements (343nm), the emission is then collected by a Maya 2000 pro spectrometer from Ocean Optics.

XPS Analysis

X-ray Photoelectron Spectroscopy (XPS) was used to study the surface chemistry of the BiOBr 10 wt%/gCN 90 wt% optimized system in comparison to that of the composing materials, namely g- C_3N_4 and BiOBr. XPS specimens were prepared by pressing a few mg of the powder samples onto high-purity indium pellets (99.99% purity). XPS data were acquired using a Kratos Axis Ultra^{DLD} spectrometer, equipped with a monochromatic Al $\text{K}\alpha$ source operated at 20 mA and 15 kV. Wide scan were acquired at a pass energy of 160 eV, energy step of 1 eV, over an analysis area of $300 \times 700 \mu\text{m}^2$. High-resolution spectra were then acquired at a pass energy of 20 eV, energy step of 0.1 eV, over the same analysis area, with a specific focus on the main signals from the elements composing the

materials, namely O 1s, C 1s, N 1s, Bi 4f, and Br 3d. The Kratos charge neutralizer system was used on all specimens; spectra have been charge corrected by setting the lowest binding-energy component of the carbon 1s spectrum to 284.8 eV. The collected data were then analysed with CasaXPS software (version 2.3.24).^[3]

Computational Modelling

We here aim at aligning the electronic energy levels of g-C₃N₄ and BiOBr with respect to the relevant reduction potentials at the semiconductor-water interface. For the former material, we employ the results of the alignment detailed in Ref 1.^[4] The latter is calculated in this work, as follows.

First, we recall that the fundamental band gap of a semiconductor at a temperature T , as calculated from first principles, $E_g^{\text{theory}}(T)$, can be defined as:

$$E_g^{\text{theory}}(T) = E_g^{\text{theory}}(0) + \Delta E_g(T),$$

where $E_g^{\text{theory}}(0)$ is calculated band gap at 0 K, usually estimated employing an electronic-structure calculation on the perfectly ordered crystalline system.^[5] For materials including heavy atoms, such as Bi and I, this calculation needs to include the effect of spin-orbit coupling (SOC), which are known to produce a sizable renormalization of the band gap in Bi-based materials, e.g. Ref. 2, $\Delta E_g(\text{SOC})$, as a consequence of the shifts in the position of the valence band maximum (VBM) and conduction band minimum (CBM), $\Delta E_{\text{VBM}}(\text{SOC})$ and $\Delta E_{\text{CBM}}(\text{SOC})$, respectively. $\Delta E_g(T)$ is the thermal band gap renormalization ensuing from atomic vibrations at finite temperatures, which has been found to be particularly significant for a plethora of systems, including fully inorganic perovskites, Bi-based semiconductors, and organic materials.^[5–7] The individual contribution to the total band gap renormalization deriving from the valence band maximum (VBM) and conduction band minimum (CBM) are similarly defined:

$$E_{\text{VBM}}^{\text{theory}}(T) = E_{\text{VBM}}^{\text{theory}}(0) + \Delta E_{\text{VBM}}(T)$$

$$E_{\text{CBM}}^{\text{theory}}(T) = E_{\text{CBM}}^{\text{theory}}(0) + \Delta E_{\text{CBM}}(T)$$

In the following, we describe the computational protocol employed to calculate band gap at room temperature from electronic-structure calculations and how to align the calculated energy levels with respect to a physical reference.

We model BiOBr and, for comparison, the oxyiodide with analogous structure, BiOI, employing a supercell approach. In particular, we consider $5 \times 5 \times 3$ tetragonal supercells with $a = b = 19.60 \text{ \AA}$, $c = 24.33 \text{ \AA}$ for BiOBr and $a = b = 20.05 \text{ \AA}$, $c = 27.42 \text{ \AA}$ for BiOI, see Figure S8, corresponding to the experimental density. Most of the calculations based on density functional theory (DFT) are carried out with the freely available CP2K/QUICKSTEP suite of programs.^[8] In this code, atomic basis sets are combined with an auxiliary plane-wave basis set to re-expand the electron density. In particular, we use the MOLOPT double-zeta polarized basis set and a cutoff of 800 Ry for the plane

waves.^[9] Core electrons are treated with the analytical Goedecker-Teter-Hutter pseudopotentials.^[10] The Brillouin zone is sampled at the sole Γ point. To properly calculate the band gap and the band edges of the materials under study, we employ a piece-wise linear hybrid functional belonging to the PBE0 family, $\text{PBE}(\alpha_K)$, developed in Ref. 10, where fractions α_K of Fock exchange equal to 23% and 24% have been found to satisfy the generalized Koopmans' condition for BiOBr and BiOI, respectively.^[11–14] We employ the auxiliary density matrix method to speed up the calculation of exact exchange in hybrid functional calculations, as implemented in CP2K, with the cFIT auxiliary basis set. Furthermore, we include non-local electron correlation via the self-consistent rVV10 scheme, to accurately describe the energetics of layered materials.^[15–17]

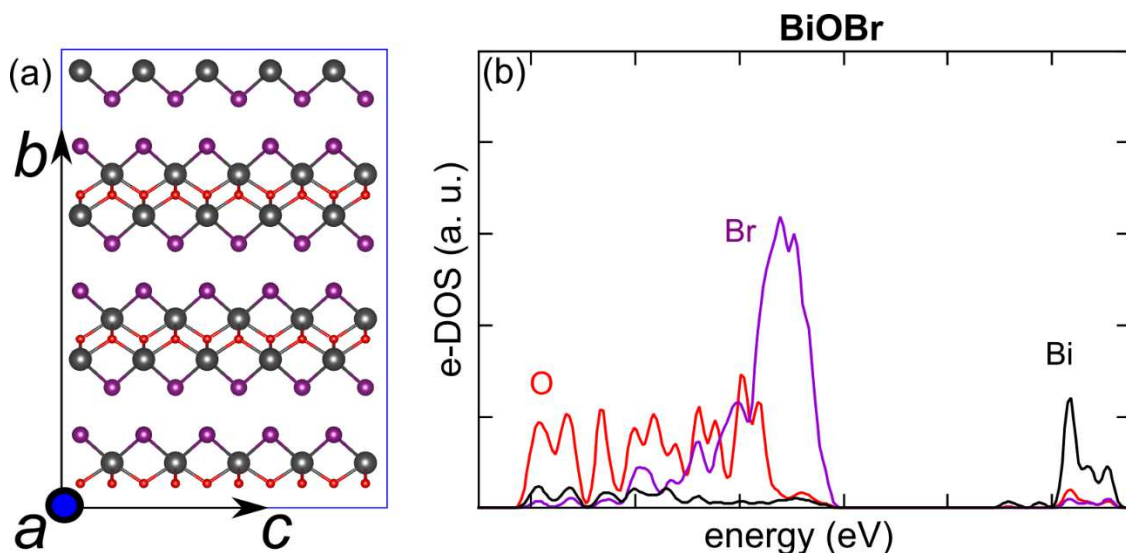


Figure S8. (a) Stick&Ball representation of the $5 \times 5 \times 3$ tetragonal supercell employed to model BiOX materials. O is in red, X=Br, I in purple, and Bi in grey. (b) Electronic density of states (e-DOS) calculated for bulk BiOBr.

Since the band edges of BiOX are dominated by the 2p states of the halogen and Bi 6s states (valence band) and Bi 6p states (conduction band), see Figure S8 (b) for BiOBr, we need to evaluate the shift of the band edges and the subsequent renormalization of the band gap induced by spin-orbit coupling.^[18] For this reason, we carry out hybrid density functional theory calculations with and without the effect within the VASP code.^[12,13,14] The calculations are performed on a 6-atom unit cell using a Γ -centered $4 \times 4 \times 4$ Monkhorst–Pack k-point mesh. The plane-wave cutoff energy is 520 eV. SOC-induced band edge shifts is computed as the difference between calculations with and without SOC. All calculations are performed at fixed experimental lattice parameters, without structural

optimization. From the difference in the absolute position of the band edges calculated with and without SOC, we infer the values of $\Delta E_g(\text{SOC})$, $\Delta E_{\text{VBM}}(\text{SOC})$, and $\Delta E_{\text{CBM}}(\text{SOC})$ for both materials, as collected in Table S1.

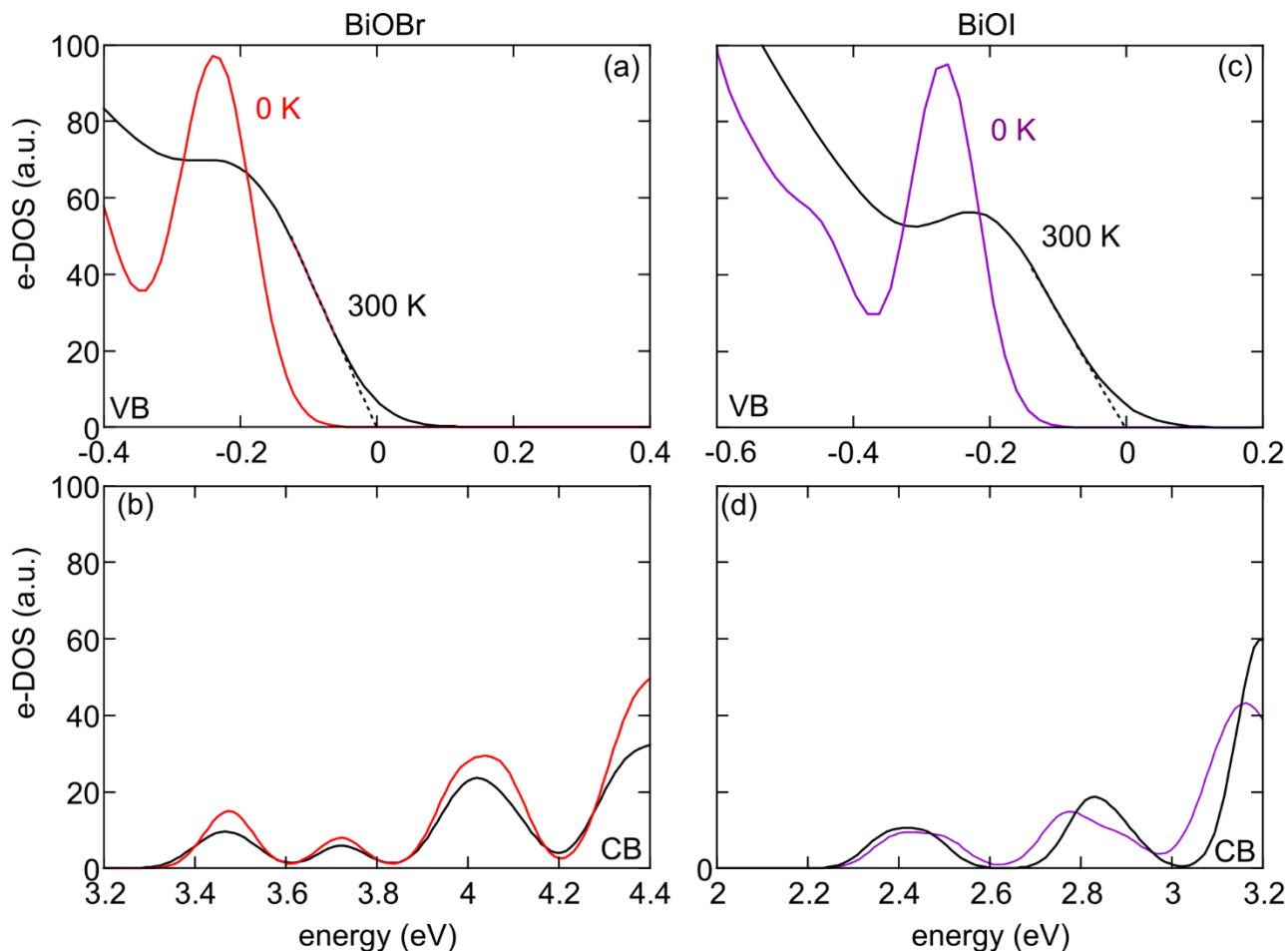


Figure S9. Electronic density of states (e-DOS) near the band edges for BiOBr (a, b) and BiOI (b, c). Black solid lines for DOS achieved from MD at 300 K. Red (purple) lines for DOS calculated from the optimized structures at 0 K of BiOBr (BiOI). For each material, energy levels are referred to the room-temperature valence band maximum, as estimated from linear extrapolation of the wing of the e-DOS.

Finally, the renormalization due to thermal motions is known to substantially impact the room-temperature band gap of a variety of semiconductors, including organic materials, halide perovskites, and Bi-based semiconductors.^[5–7] For this reason, we perform molecular dynamics (MD) simulations with CP2K/QUICKSTEP using the same computational set-up described above. MD runs in the canonical NVT ensemble, ensured by the use of the thermostat developed by Nosé and Hoover, are carried out for 10 picoseconds, with a time-step of 1 fs.^[22,23] We then employ a linear extrapolation of the wings of the electronic density of states (DOS) near the band edges. The difference in the band

edges calculated at 0 K and those achieved from the MD simulation at 300 K provides us with the estimated values of $\Delta E_g(T)$, $\Delta E_{\text{VBM}}(T)$, $\Delta E_{\text{CBM}}(T)$ cf. Figure S9 and Table S1. The slightly larger value observed for BiOI can be ascribed to the wider thermal fluctuations of the Bi-I bonds, as evidenced by the calculated radial distribution functions in Figure S10.

Table S1. Calculated values of the SOC and thermal corrections to the band edges and to the fundamental band gap of the considered BiOX semiconductors. All values are given in eV.

Correction	BiOBr	BiOI
$\Delta E_{\text{VBM}}(\text{SOC})$	+0.02	+0.12
$\Delta E_{\text{CBM}}(\text{SOC})$	−0.21	−0.20
$\Delta E_g(\text{SOC})$	−0.23	−0.32
$\Delta E_{\text{VBM}}(T)$	+0.12	+0.14
$\Delta E_{\text{CBM}}(T)$	−0.05	−0.12
$\Delta E_g(T)$	−0.17	−0.26

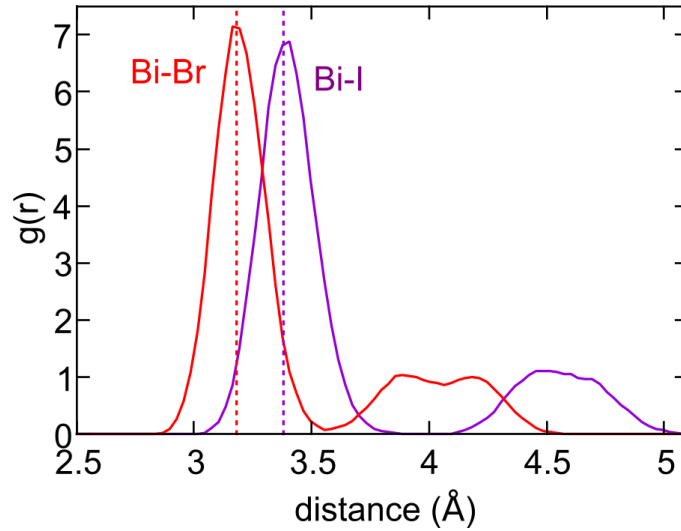


Figure S10. Bi-X radial distribution functions (X=I, Br) as calculated from MD simulations of BiOX materials. Bi-Br in violet, Bi-I in red. Vertical dashed line represent the lengths of Bi-X bonds for the respective optimized 0 K atomistic models.

To align the calculated band edges with respect to a physical reference, we model BiOX-vacuum interfaces. In particular, we construct atomistic slabs of BiOBr and BiOI, considering two different stoichiometric symmetric systems: the (001) and the (010) surfaces. The bulk-like (001) surface is cut in parallel with respect to the BiOX layered planes and it is BiX-terminated with no undercoordinated atoms, as illustrated in Figure 6. The slab has $a = b = 15.68 \text{ \AA}$, $c = 70.00 \text{ \AA}$ for

BiOBr and $a = b = 16.04 \text{ \AA}$, $c = 70.00 \text{ \AA}$ for BiOI (including, for both BiOBr and BiOI, $\sim 30 \text{ \AA}$ of vacuum) and consists of 5 BiOX layers. We note that for the (001) surface, we also tested O-terminated surfaces, which, however, resulted in unstable systems, with disruption of the terminal unsaturated layers. The same occurred when considering O-H covered, i.e. hydroxylated, slabs.

At variance with this, the stoichiometric (010) slab displays a BiOX-terminated surface perpendicular to the direction of the layered planes and features undercoordinated atoms, cf. Figure 6. The dimensions of the periodic slabs are $a = 16.22 \text{ \AA}$, $b = 15.68 \text{ \AA}$, $c = 75.00 \text{ \AA}$ for BiOBr and $a = 18.22$, $b = 16.04 \text{ \AA}$, $c = 75.00 \text{ \AA}$ for BiOI, again with a vacuum layer of $\sim 30 \text{ \AA}$, separating the periodic replicas along the z direction. For each slab, we carry out a full geometry relaxation at the PBE(α_K)+rVV10 level of theory.

The surface energies of the slabs are calculated according to the following expression:

$$\gamma = \frac{(E_{\text{slab}} - N \times E_{\text{bulk}})}{2A} ,$$

where E_{slab} is the total energy of the slab, E_{bulk} the total energy *per atom* of the bulk, and A is the surface area of the slab model. As reported in Table S2, surface energies are found to amount to 0.011 and 0.048 eV/ $\text{\AA}^2$ for the (001) and the (010) surface models of BiOBr, respectively. Similar values of 0.011 and 0.028 eV/ $\text{\AA}^2$ are estimated for BiOI surfaces, which, however, shows a reduced difference between the two surface terminations.

Table S2. Calculated values of the surface energy γ from atomistic modelling of the (001) and the (010) surfaces for the BiOX semiconductors under consideration. Values are given in eV/ $\text{\AA}^2$.

	BiOBr	BiOI
γ_{001}	0.011	0.011
γ_{010}	0.048	0.028

For each slab, we determine the plane-averaged electrostatic-potential along the z direction, to refer the calculated band edges with respect to the vacuum level. No residual electrical field is observed in the studied slabs, as evidenced by the flat potential across the vacuum region shown in Figure S11. Finally, we align the calculated energy levels also with respect to the standard hydrogen electrode (SHE), since redox potentials are usually reported on this energy scale. In particular, for internal consistence, we employ a computational SHE detailed in Refs. 24 and 25, which is found 4.56 eV below the vacuum level, in excellent accord with the experimental estimate proposed by Trasatti (4.44

eV).^[24–26] The alignment scheme presented in Fig. 7 of the main text is completed including the experimental reference values for N₂/NH₃ and O₂/H₂O redox levels.

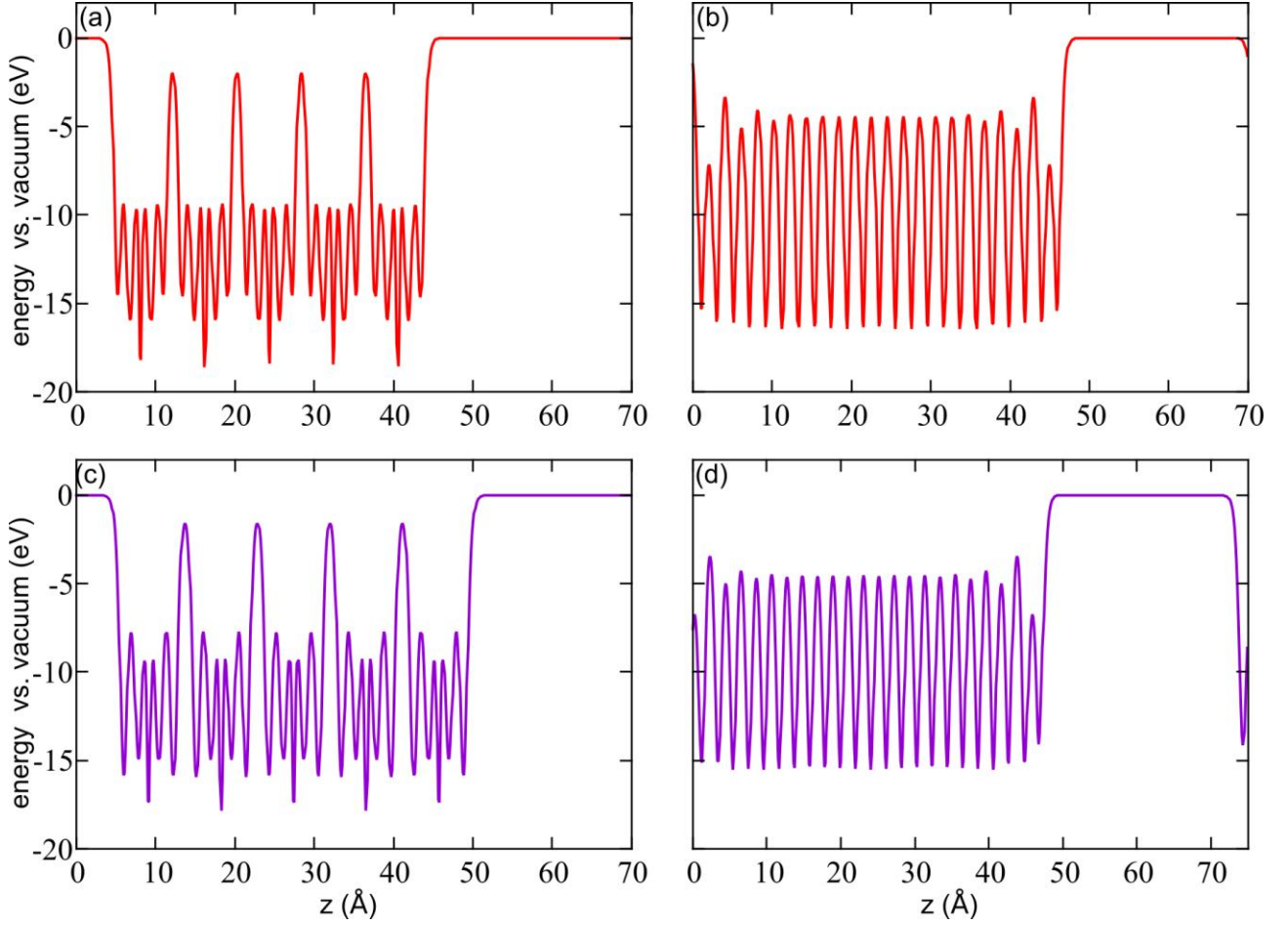


Figure S11. Average electrostatic potential referred to the vacuum level across the semiconductor-vacuum interface for BiOBr and BiOI (red and purple lines respectively). Panels (a) and (c) for models of (001) surface while panels (b) and (d) illustrate the potential profile for (010) slabs.

In the main text, we also report the energy level associated with surface polarons on the (010) surface. The binding energy of the electron polaron is defined as:

$$E_b^-(\text{pol}) = E_{\text{slab}}^-(\text{pristine}) - E_{\text{slab}}^-(\text{pol})$$

where $E_{\text{slab}}^-(\text{pol})$ is the total energy of the charged slab with the polaronic distortion, while $E_{\text{slab}}^-(\text{pristine})$ the total energy of the charged pristine slab. A positive value of the quantity corresponds to favorable polaronic localization. The redox level (0/−1) associated with the polaron, $\mu(0/-1)$, is placed at an energy $E_b^-(\text{pol})$ below the position of the conduction band maximum, ϵ_{CBM} , of the material, i.e.:

$$\mu(0/-1) = \epsilon_{\text{CBM}} - E_b^-(\text{pol})$$

The co-author Giulia Giovilli, author of the present Ph.D. work, synthesized and characterized BiOBr, g-C₃N₄ and the g-CN/BiOBr heterojunctions series, and carried on the PNF experiments.

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Chapter 3

Synthesis and Characterization of g-C₃N₄/Metal NPs Based Composites for the Photocatalytic Production of Hydrogen

Letizia Sensalari, Giulia Giovilli,^a Lavinia Doveri^a, Yuri Hernandez-Diaz^a and Lorenzo Malavasi^a

^aDepartment of Chemistry and INSTM, University of Pavia, Via Taramelli 16, Pavia, 27100, Italy

Abstract

Metallic NPs (Ag and Au) decorated g-C₃N₄ nanosheets were synthesized starting with the exfoliation of bulk g-C₃N₄ either by liquid sonication or thermal treatment (at different temperatures); then the obtained nanosheets were functionalized with thiol group (-SH); in the end, both functionalized and non-functionalized g-C₃N₄ NSs were decorated using Ag and Au nanoparticles (nanospheres and nanorods) through co-precipitation, with different loadings of metal nanoparticles (1, 0.4, 0.1 wt%). The optimal water-splitting performance, with hydrogen evolution rate of $\sim 70 \mu\text{mol g}^{-1} \text{ h}^{-1}$, is achieved by coupling g-C₃N₄ NSs (thermally exfoliated at 525°C) with 0.1% of Ag nanoparticles and no surface thiols functionalization. Thermal exfoliation enhances the photocatalytic activity of the heterojunction even in the presence of very low quantities of Ag NPs; the higher number of surface defects means more attack sites for nanoparticles, but also more active sites for the activation of nitrogen molecules and their subsequent reduction. The surface is also more homogeneously covered in nanoparticles than when thiol groups are present.

1. Introduction

With its high gravimetric energy content (143 MJ kg^{-1}) and its zero greenhouse-gas emission, Hydrogen has emerged in recent years as a promising energy carrier; it can be used for storing the surplus energy coming from renewable energy sources and, acting as carbon-free fuel, across various sectors (energetic, transport, industrial).

A roadblock that slows down its implementation on a larger scale is its production: only 4% of hydrogen produced globally comes from carbon-free source (electrolytical water-splitting), and fossil fuels are still the most common industrial source of hydrogen. 48% of the total H_2 produced is made through methane-steam reforming (MSR), still the cheapest production method available on an industrial scale.^[1]

Producing green hydrogen through photocatalytic water-splitting is a field of research that has been garnering the interest of the scientific community thanks to its environmental sustainability, limited energetic consumption and low cost: water is a carbon-free hydrogen source and solar light is the only energy required.

One of the biggest challenges of this production method is requiring a efficient photocatalyst that can carry on this reaction. It has to: be water-stable, absorb in the visible range, have a band gap and band positions compatible with the redox potential of water-splitting reactions, produce charge carriers and keep them separated enough for the reactions to happen.^[2]

A photocatalyst that answers many of these requests and, thanks to that, has been the focus of much research in the last decade is graphitic carbon nitride, or $\text{g-C}_3\text{N}_4$. Used for the first time by Wang et al. in 2009, $\text{g-C}_3\text{N}_4$ is a polymeric *n-type* semiconductor, with a bidimensional structure akin to graphene and made of C (sp^2 hybridization), N and a small quantity of H impurities; it shows high thermal stability and insolubility in a majority of solvents.

The number of different nitrogen-rich precursors that can be used in the synthesis of g-C₃N₄ is high (some examples are urea, dicyandiamide and melamine), and their pyrolysis is carried on between 500 and 600°C either in air or in inert atmosphere. The presence of small quantities of hydrogen impurities are a sign that the pyrolysis is never 100% complete; the resulting structure enhances the photocatalytic activity of the material thanks to surface defects that make it rich in electrons and hydrogen bonds.

Additionally, to increase further its activity, the low surface area of bulk g-C₃N₄ ($\approx 10 \text{ m}^2/\text{g}$) can be increased by cleaving the Van der Waals bonds that keep the material's layers together.

g-C₃N₄ absorbs in the visible light range ($\lambda > 420\text{nm}$) in virtue of its band gap (centered around 2.7 eV) – broad enough to take into account both the endothermic character of the reaction and its overpotential – and its band positions, that are conducive to photocatalytic water-splitting.

The biggest draw-back of g-C₃N₄ is the recombination speed of the photogenerated electron-hole couples being higher than HRR (Hydrogen Reduction Reaction): once promoted to the conductive band, electrons quickly decay back into the valence band, filling back up the holes they left. Only the surviving couples are transported to the active sites by diffusion processes or electric fields, to take part in the reactions.^[3,4]

Together with a sacrificial agent used to trap holes and make them unavailable for the recombination process, a co-catalyst is also added to the reaction environment – usually metallic Pt – to further enhance the photocatalytic activity of g-C₃N₄. A similar role can be played by the noble metal nanoparticles (NPs) that decorate g-C₃N₄: a heterojunction built this way does not ideally need the addition of a co-catalyst.

Noble metals have a lower Fermi level than the semiconductor and, because of that, they help separating charge carriers: conduction-band electrons seek these energetic levels, therefore physically moving towards metallic nanoparticles. On the surface of g-C₃N₄, metallic NPs create a charge-

separating region called Schottky barrier: the potential difference created directs electrons and holes towards opposite directions, with electrons being attracted to the metallic nanoparticles, to balance the Fermi levels at the interface of the two.^[5,6]

Thanks to their nanometric size, metal NPs are affected by an optic phenomenon called localized surface plasmon resonance (LSPR): when an electromagnetic radiation interacts with nanosized particles, the electronic photoexcitation induces a oscillation of electrons, with subsequent formation of a strong electric field on the surface of the material. The LSPR absorption band shows up when the incident photons' frequency resonates with the typical surface plasmon's frequency of the nanostructure (depending on type, size and morphology), increasing the light absorbed by the material.

The aim of this work has been to investigate Ag and Au as cheaper co-catalyst alternative than Pt through the utilization of their metallic NPs to decorate g-C₃N₄ nanosheets: in comparison to published literature, we carried of a systematic investigation on how the hydrogen yield produced by photocatalytic water-splitting under simulated solar light is affected by tuning different variables, like the type, shape and quantity of metallic NPs, the presence or lack thereof of surface functionalization, and the method and temperature used in the synthesis of g-C₃N₄ nanosheets.

2. Result and Discussion

The size and concentration of Ag nanoparticles (Ag NPs), synthesized according to the experimental procedure reported in the Supporting Information (SI), have been determined through multi-angle dynamic light scattering (MADLS) and UV-Vis spectroscopy: Ag nanoparticles show an absorption band at 425 nm (corresponding to a diameter of 40 nm) and MADLS measurements confirm their diameter range, between 40 and 45 nm, and their concentration, around $10^{10} - 10^{11}$ particles mL^{-1} .

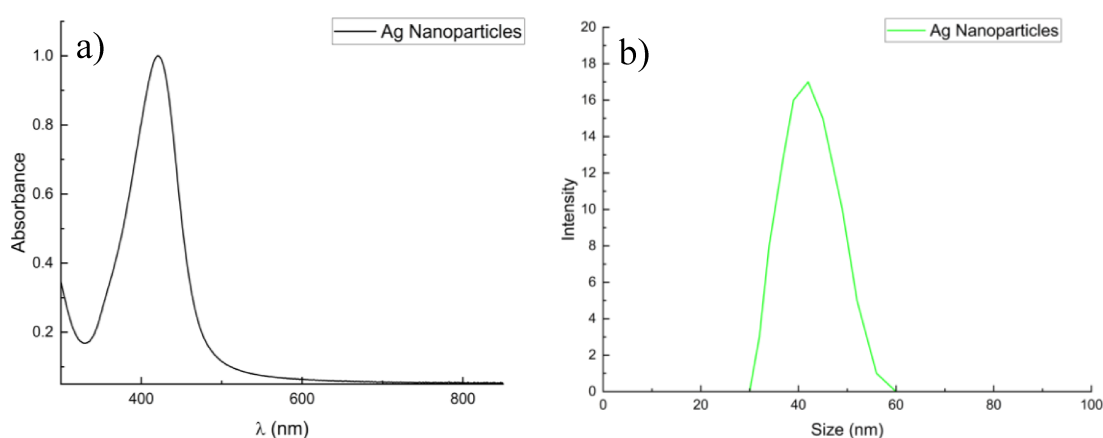


Figure 1. a) UV-Vis Absorption and b) MADLS Spectra of Ag NPs

The Ag decorated $\text{g-C}_3\text{N}_4$ and $\text{SH-g-C}_3\text{N}_4$ nanosheets systems (respectively non-functionalized and functionalized with thiol groups, SH) have been synthesized according to the experimental procedure reported in the Supporting Information (SI) which is schematically represented in Figure 2. Weight ratios between Ag and $\text{g-C}_3\text{N}_4$ investigated are (wt% of Ag) 1, 0.4, and 0.1.

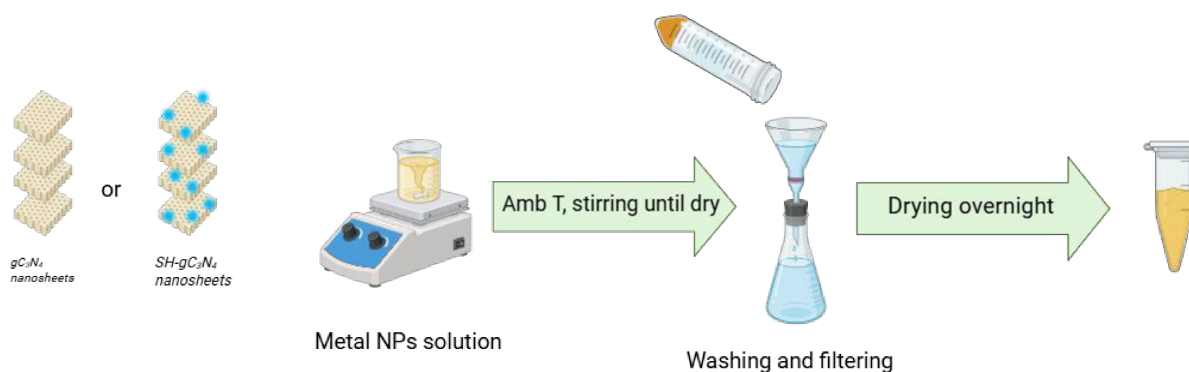


Figure 2. Schematic illustration of the synthetic procedure to obtain the Ag/g- C_3N_4

The X-ray diffraction (XRD) patterns of the different compositions are reported in Figure 3a (g-C₃N₄ nanosheets) and 3b (SH-g-C₃N₄ nanosheets). Figure 3c report the comparison between the patterns of pristine g-C₃N₄.

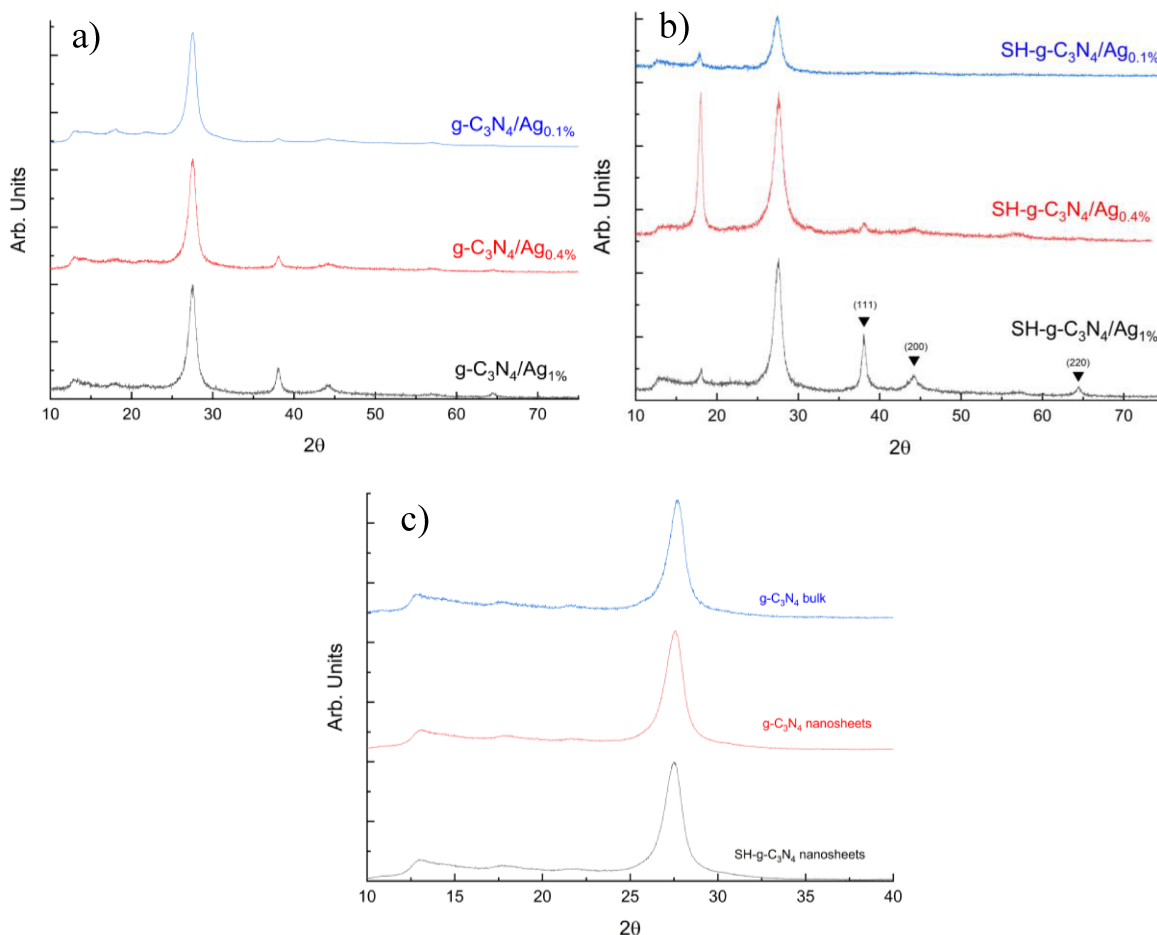


Figure 3. a) XRD patterns of g-C₃N₄/Ag as a function of Ag wt%; b) XRD patterns of SH-g-C₃N₄/Ag as a function of Ag wt%; c) XRD patterns of pristine bulk, exfoliated and functionalized g-C₃N₄

The presence of Ag nanoparticles, with a typical FCC structure (space group $Fm-3m$), can be seen from Figure 2A and 2B, thanks to the presence of peaks at 38°, 44° and 65° corresponding to the (111), (200) and (220) reflections.^[7] The peaks' intensity increases with Ag wt%. The diffraction patterns of pure g-C₃N₄ (figure 2C) show the typical broad peaks around 13° and 28° corresponding to the (100) and (200) reflections^[8] and, when functionalized with thiol groups, a peak with variable intensity around 18, assigned to the (110) reflection.^[9]

EDX maps (Figure S1 and S2) were recorded to show the distribution of Ag NPs on the surface of g-C₃N₄ and SH-g-C₃N₄: the two samples differ in the fact that the presence of the thiol groups on the surface lead to the formation of agglomerates of nanoparticles, thanks -SH being a preferential site of interaction, while the non-functionalized g-C₃N₄ show a much more homogenous distribution of NPs, even if lower in quantity.

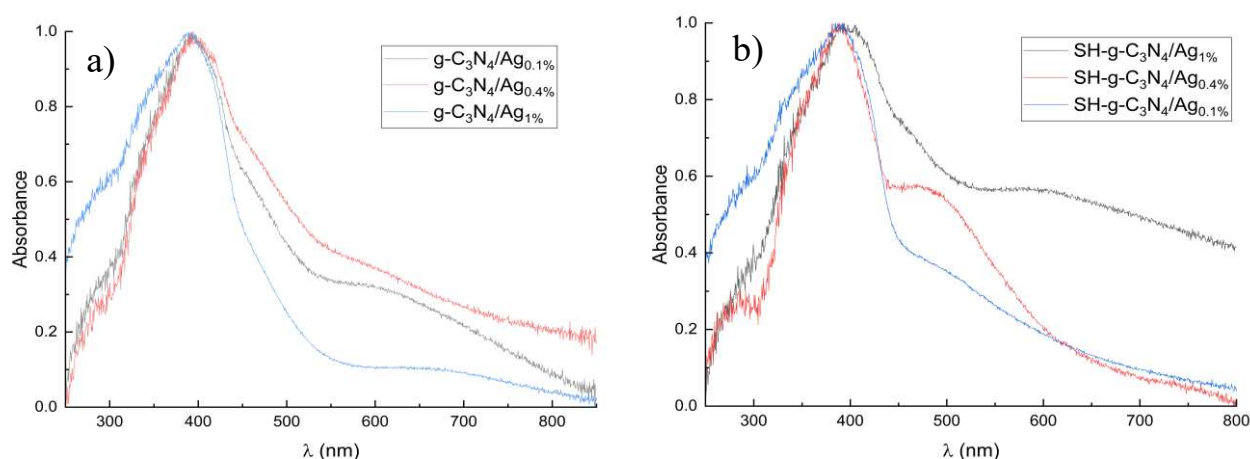


Figure 4. Absorption spectra of the a) g-C₃N₄/Ag system and of the b) SH-g-C₃N₄/Ag system

All six samples present a wide absorption in the Vis range: the absorption band localized around 400 nm coincide with that of non-functionalized g-C₃N₄, while the surface plasmon resonance (SPR) of Ag NPs and the resulting charge transfer to g-C₃N₄ is the cause of the wide absorption band from 400 to 750 nm.^[7] It's possible to see how the SPR effect is higher for the highest Ag wt%. The indirect band gap of pure g-C₃N₄ nanosheets (both functionalized and non-functionalized) is around 2.73 eV, in agreement with previous experimental and computational studies.

Figure 5 reports the results in terms of hydrogen evolution rates, expressed ad μmol g⁻¹h⁻¹, obtained by photocatalytic experiments under simulated solar light in absence of Pt co-catalyst. Experimental details for the photocatalytic trials are provided in the SI.

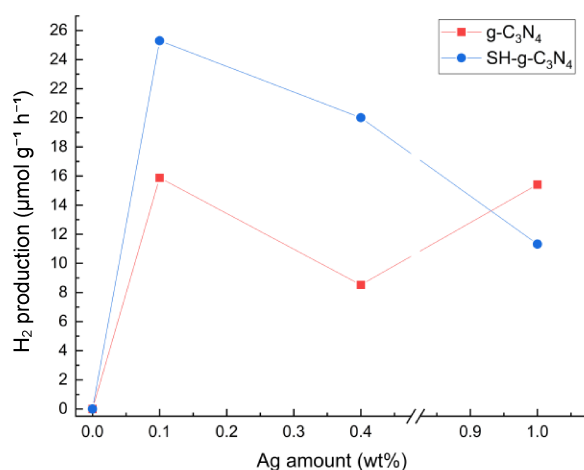


Figure 5. Hydrogen production as a function of Ag wt% in the systems made with functionalized (blue) and non-functionalized (red) g-C₃N₄

The data (Table S1) reported in Figure 5 shows that, for all six samples, in absence of Pt, the Ag decoration is enough to enhance hydrogen production: a comparison between the two systems demonstrate that functionalized heterojunctions' production decreases with the increase of Ag NPs, while non-functionalized heterojunctions present a minimum production corresponding to 0.4% Ag NPs, while 0.1 and 1% are mostly the same. In both cases, Ag (0.1%) shows the highest hydrogen production (respectively 15.9 $\mu\text{mol g}^{-1} \text{h}^{-1}$ for g-C₃N₄ and 25.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$ for SH-g-C₃N₄), a good result in terms of sustainability of the system presented.

To further enhance hydrogen production, systems containing Ag (0.1%) and thermally exfoliated g-C₃N₄ (the experimental procedure can be found in the SI) at three different temperatures – 500, 525 and 550°C – were investigated. The thermally exfoliated g-C₃N₄ (T, where T = 500, 525 or 550°C) nanosheets were further functionalized to produce SH-g-C₃N₄(T).

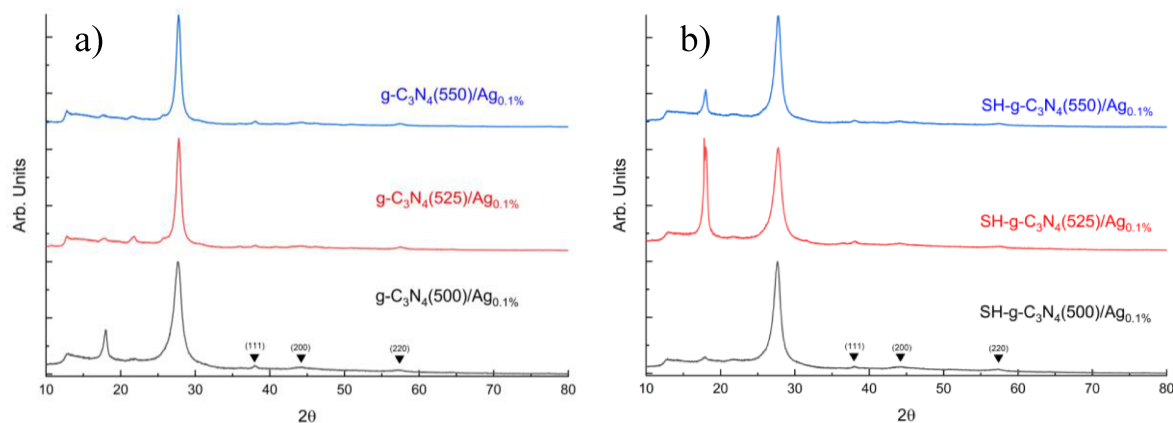


Figure 6. XRD Patterns of the a) g-C₃N₄(T)/Ag_{0.1%} and b) SH-g-C₃N₄(T)/Ag_{0.1%} systems

XRD patterns of the thermally exfoliated samples show the same structure previously seen for the liquid exfoliated ones (Figure 6) while the UV-Vis spectra (Figure 7) show a decreased absorption in the 450-750 nm range: we expect this lowered absorption to impact the photocatalytic activity, shown in Figure 8 (Table S2)

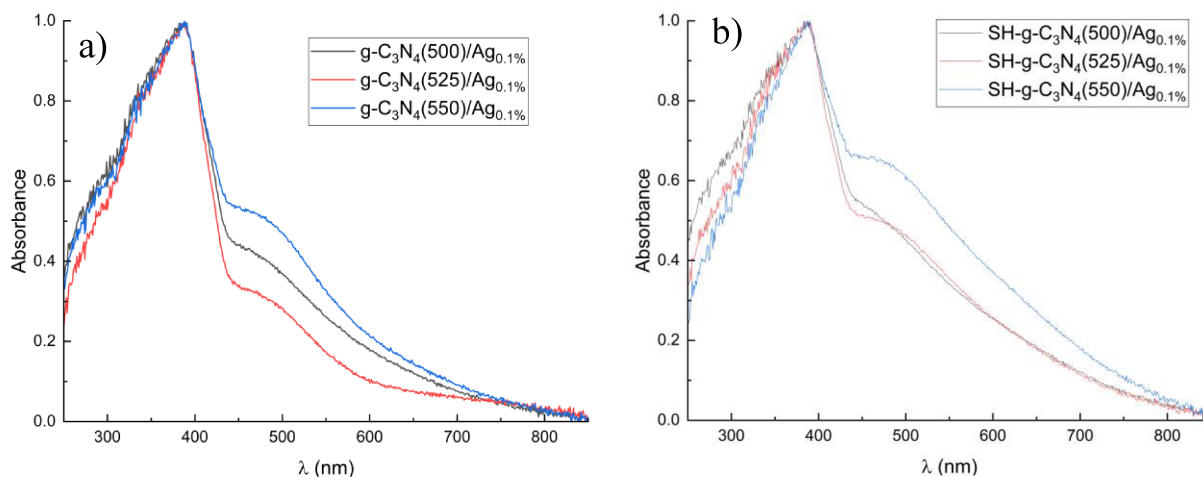


Figure 7. UV-Vis Absorption Spectra of the a) $\text{g-C}_3\text{N}_4(\text{T})/\text{Ag}_{0.1\%}$ and b) $\text{SH-g-C}_3\text{N}_4(\text{T})/\text{Ag}_{0.1\%}$ systems

An interesting trend emerges from this investigation: the $\text{g-C}_3\text{N}_4(\text{T})/\text{Ag}_{0.1\%}$ system shows an increased hydrogen production, while the production of $\text{SH-g-C}_3\text{N}_4(\text{T})/\text{Ag}_{0.1\%}$ system is lower than the best-performing yield previously recorded ($25.3 \mu\text{mol g}^{-1} \text{h}^{-1}$). For both systems, the best-performing exfoliation T corresponds to 525°C (respectively $69.6 \mu\text{mol g}^{-1} \text{h}^{-1}$ for $\text{g-C}_3\text{N}_4$ and $20.9 \mu\text{mol g}^{-1} \text{h}^{-1}$ for $\text{SH-g-C}_3\text{N}_4$).

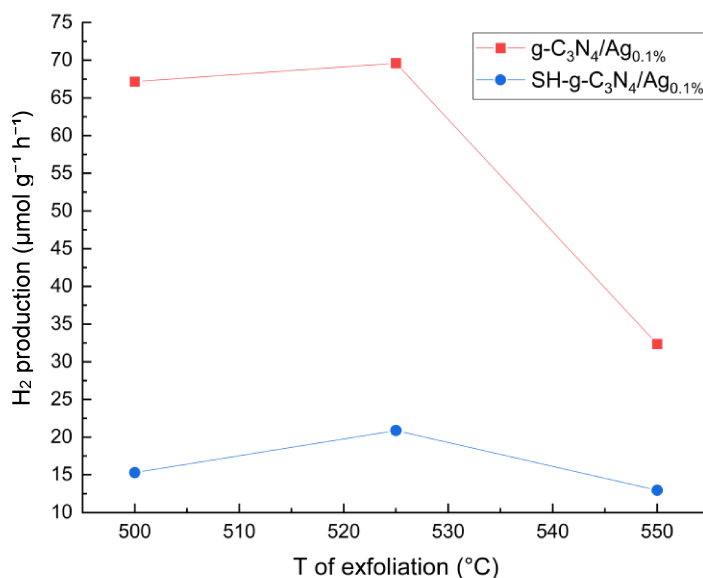


Figure 8. Hydrogen production as a function of T of exfoliation in the systems made with functionalized (blue) and non-functionalized (red) $\text{g-C}_3\text{N}_4/\text{Ag}_{0.1\%}$

This increased yield can be explained by the fact that thermal exfoliation not only reduces g-C₃N₄ thickness by removing layers from the bulk structure, but it also introduces carbon and nitrogen defects (CD and ND) by destroying the hydrogen bonds that keep the conjugated rings connected. In the presence of several non-saturable N-atoms, that act as the absorbing photoelectron and paramagnetic core of the CDs-gC₃N₄ covalent connection, CDs in g-C₃N₄ may significantly limit charge recombination^[10], and improve the photocatalytic and adsorption capacities of g-C₃N₄ by adjusting their physicochemical features.^[11] NDs seem effective in narrowing the intrinsic energy bandgap to broaden the Vis light absorption^[12] and in reducing charge recombination by acting as either electron or hole capture^[13], but also they function as an active sites that facilitates quick photoelectronic exchange with the subsequent redox reaction.^[10]

The highest the temperature used during exfoliation, the thinner are the nanosheets obtained: an increased exfoliation carries with itself an increase in porosity (more vacancies, thus more active sites) and in superficial area (increased contact area between photocatalyst and reagents), enhancing its photocatalytic activity. A higher exfoliation also comes with a narrowing of the Vis-light absorption range: the change is easily appraised by the naked eye, because the colour of g-C₃N₄ goes from strong yellow to off-white as the exfoliating temperature increases.^[5]

SEM images (Figure S3) captured of the g-C₃N₄(T)/Ag_{0.1%} shows how much the morphology of the material depends on T: the highest it is, the more cracks and pores litter the surface. EDX maps of these same materials were captured to determine the spatial distribution of Ag NPs: in a similar way, the higher the T and the more defects and pores present, the more nanoparticles decorate the surface, enhancing the activity of the photocatalyst. Although, as we can see in the case of T = 550°C, when too much surface is covered by Ag NPs, the hydrogen produced by the heterojunction plummets, because a bigger number of pores and vacancies present the nanosheets' surface are occupied by NPs and thus can't function as activation sites for NH₃.

$\text{g-C}_3\text{N}_4(525^\circ\text{C})/\text{Ag}_{0.1\%}$ is the best compromise between a highly exfoliated semiconductor and a highly decorated system, enhancing thus the overall photocatalytic activity of the composite.

To determine if Ag NPs can be used as a substitute of Pt, the pure thermally exfoliated $\text{g-C}_3\text{N}_4(\text{T})$, with $\text{T} = 500, 525$ and 550°C , was used in hydrogen production experiments in the presence of 0.1% Pt as a co-catalyst (experimental details for the photocatalytic trials are provided in the SI). The results (Table S3), reported in figure 9, show both systems following the same trend, with 525°C being the exfoliating temperature yielding the best results: $\text{g-C}_3\text{N}_4(525^\circ\text{C})/\text{Pt}_{0.1\%}$ shows up as the overall best-performing sample ($293.5 \mu\text{mol g}^{-1} \text{h}^{-1}$), even when it's compared with $\text{g-C}_3\text{N}_4(525^\circ\text{C})/\text{Ag}_{0.1\%}$ ($69.6 \mu\text{mol g}^{-1} \text{h}^{-1}$). The hydrogen yield of $\text{g-C}_3\text{N}_4(525^\circ\text{C})/\text{Pt}_{0.1\%}$ is also notably higher than the one of $\text{g-C}_3\text{N}_4(525^\circ\text{C})/\text{Pt}_{1\%}$ ($143.4 \mu\text{mol g}^{-1} \text{h}^{-1}$).

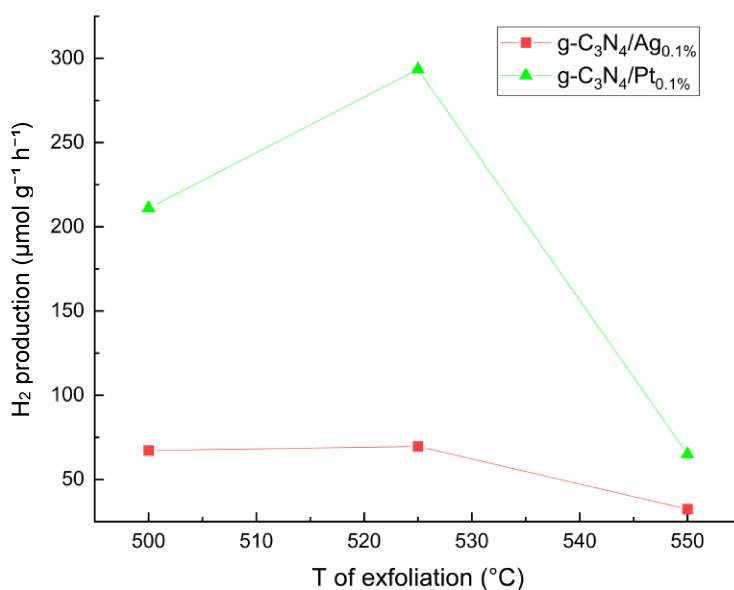


Figure 9. Hydrogen production as a function of T of exfoliation in the systems containing $\text{Ag}_{0.1\%}$ (red) and $\text{Pt}_{0.1\%}$ (green)

To investigate the effect of LSPR on the hydrogen yield, we switched Ag NPs with Au nanospheres (NS) and nanorods (NR). The two different Au nanostructures and $\text{g-C}_3\text{N}_4(525)/\text{Au}_{0.1\%}$ system were synthesized according to the experimental procedure reported in the Supporting Information (SI).

Figure 10a shows the UV-Vis Absorption spectra of the two nanostructures: Au nanospheres show one peak at 518 nm, while the nanorods present two bands, at 525 and 640 nm, corresponding

to the LSPR effect along the length and the height of the bidimensional structure. MADLS measurements are reported (figure 10b) only for Au nanospheres, because the technique's not reliable enough to determine the size of asymmetric nanostructures.

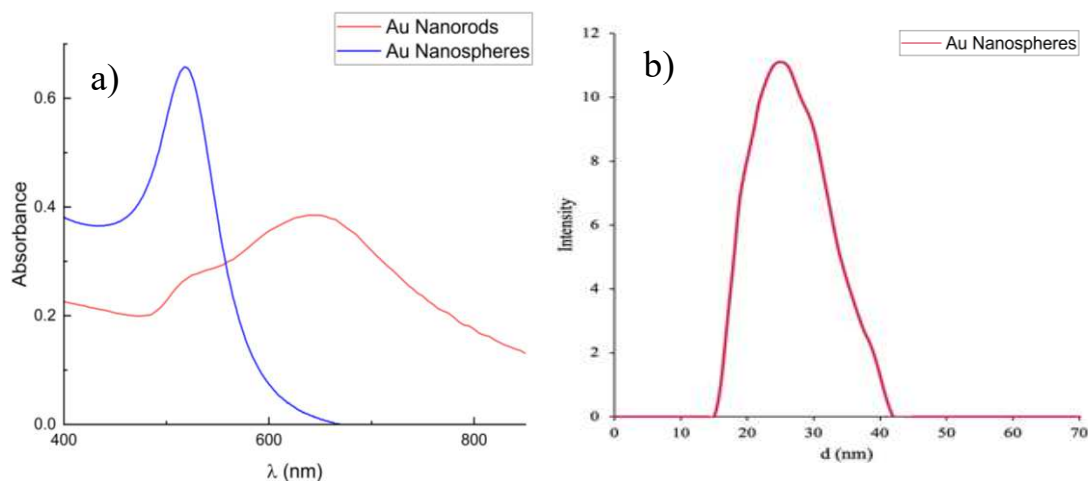


Figure 10. a) UV-Vis Absorption and b) MADLS spectra of Au nanostructures

Figure 11a the diffraction patterns of the $g\text{-C}_3\text{N}_4(525)/\text{Au}_{0.1\%}$ system show the characteristic structure of $g\text{-C}_3\text{N}_4$ with peaks at 13° and 27° , and additional weaker peaks 18° , 22° and 57° associated to the (110), (111) and (004) reflections.^[9] The peaks at 38° and 44° are associated to the presence of nanostructured Au (both NR and NS), respectively to the (111) and (200) planes of a face-centered cubic structure (an enlarged view of these peaks can be seen in Figure S5).^[14,15]

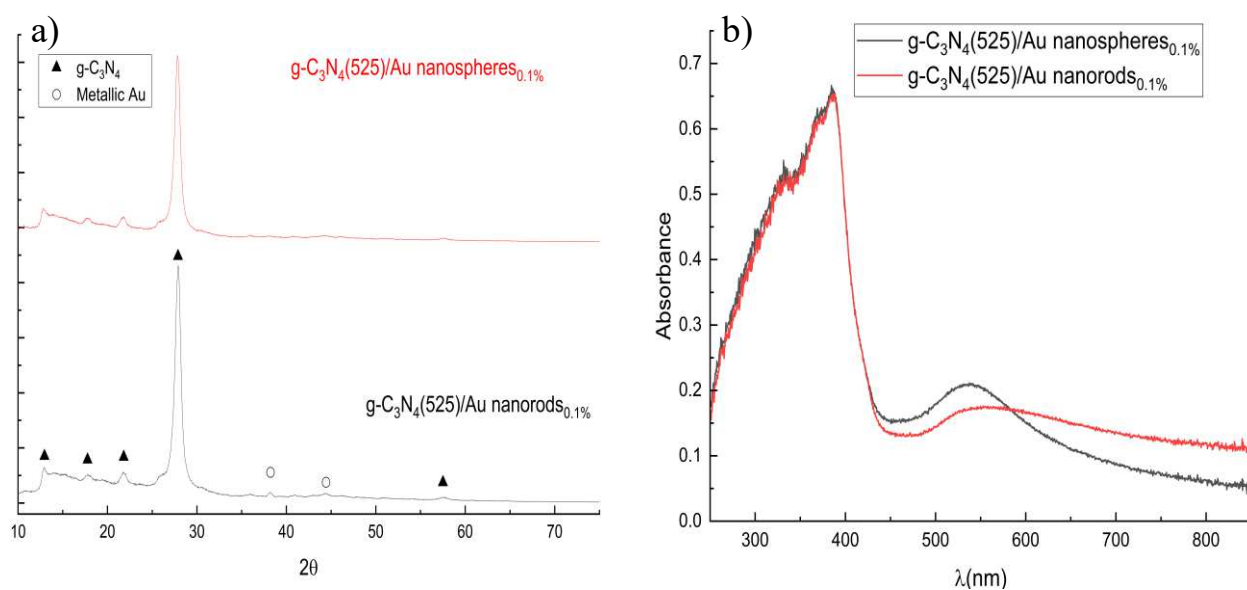


Figure 11. a) XRD patterns and b) UV-Vis Absorption spectra of the $g\text{-C}_3\text{N}_4(525)/\text{Au}_{0.1\%}$ system

In figure 11b we can see the UV-Vis spectra of the g-C₃N₄(525)/Au_{0.1%} system: g-C₃N₄ typical absorption band is still present at 400 nm and, depending on the Au nanostructure used to decorate the material, there's a second absorption band: for nanospheres centered around 550 nm (consistently with what we see for Au NS when in solution), and for nanorods there's a broader band starting from 500 nm and slightly decreasing in intensity from 650 nm.

Table S4 reports the hydrogen production of the g-C₃N₄(525)/Au_{0.1%} system when compared with g-C₃N₄(525°C)/Ag_{0.1%}; the photocatalytic hydrogen production is two times (44.7 $\mu\text{mol g}^{-1} \text{h}^{-1}$) and four times (20.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$) lower for NS and NR respectively. A SEM image (Figure S4) of g-C₃N₄(525°C)/Au-NS_{0.1%} shows how Au NS cover homogenously the surface of graphitic carbon nitride, but the overall coverage is much lower when compared with the same sample decorated with Ag.

3. Conclusions

In this study, we have systematically investigated the photocatalytic water-splitting performance under simulated solar light of g-C₃N₄ decorated with metallic nanoparticles to enhance the hydrogen yield of the material. The results demonstrate that decorating the surface of graphitic carbon nitride with metallic nanoparticles actually results in an enhancement of its photocatalytic activity, and that the hydrogen yield can be tuned through: (i) different exfoliating methods, (ii) functionalization or lack thereof for g-C₃N₄, and (iii) nanoparticles decoration (different metals, nanostructure and wt%).

The optimal performance is achieved with g-C₃N₄(525°C)/Ag_{0.1%}, with a hydrogen evolution rate of $\sim 70 \mu\text{mol g}^{-1} \text{h}^{-1}$: the enhanced photocatalytic activity of thermally exfoliated nanosheets means that the material makes better use of the lower quantity of NPs when compared with liquid exfoliated ones. Spread out defects covering the surface of g-C₃N₄ are a better site of deposition for NPs than the thiol groups used to functionalize the material, because they produce a less intense and more homogenous decoration of the surface: too many nanoparticles tend to decrease the amount of

light absorbed by the material, weakening its photocatalytic activity. Switching Ag NPs with Au NPs lowers the hydrogen yield: the amount of Au nanoparticles that cover g-C₃N₄ is low enough to result in a lower light absorption, and thus in a decreased photocatalytic activity.

This work highlights the importance of the subsequent tuning of different physicochemical characteristics to build an optimized heterojunction for photocatalytic applications: functionalization, porosity, thickness, surface area, presence of vacancy, metallic nanoparticles (type of metal and morphology), weight ratio, and homogeneity of coverage all have an effect on the photocatalytic hydrogen yield. In addition, this work shows that metallic NPs can be used in substitution of Pt co-catalyst, because their presence enhances the hydrogen production of the pure g-C₃N₄ nanosheets, even if further research is necessary to find a configuration that yield similar results.

Supplementary information

	<i>Ag(1%)</i>	<i>Ag(0.4%)</i>	<i>Ag(0.1%)</i>
<i>g-C₃N₄</i>	15.4	8.5	15.9
<i>SH-g-C₃N₄</i>	11.3	20	25.3

Table S1. Hydrogen yields ($\mu\text{mol g}^{-1} \text{h}^{-1}$) produced by *g-C₃N₄/Ag_x* e *SH-g-C₃N₄/Ag_x*

	<i>500°C</i>	<i>525°C</i>	<i>550°C</i>
<i>g-C₃N₄(T)/Ag_{0.1%}</i>	67.2	69.6	32.4
<i>SH-g-C₃N₄(T)/Ag_{0.1%}</i>	15.3	20.9	12.9

Table S2. Hydrogen yields ($\mu\text{mol g}^{-1} \text{h}^{-1}$) produced by *g-C₃N₄(T)/Ag_{0.1%}* e *SH- g-C₃N₄(T)/Ag_{0.1%}*

	<i>500°C</i>	<i>525°C</i>	<i>550°C</i>
<i>g-C₃N₄(T)/Pt_{0.1%}</i>	211	293.5	65

Table S3. Hydrogen yields ($\mu\text{mol g}^{-1} \text{h}^{-1}$) produced by *g-C₃N₄(T)/Pt_{0.1%}*

	<i>Nanorods</i>	<i>Nanospheres</i>
<i>g-C₃N₄(525)/Au_{0.1%}</i>	20.3	44.7

Table S4. Hydrogen yields ($\mu\text{mol g}^{-1} \text{h}^{-1}$) produced by *g-C₃N₄(525)/Au_{0.1%}*

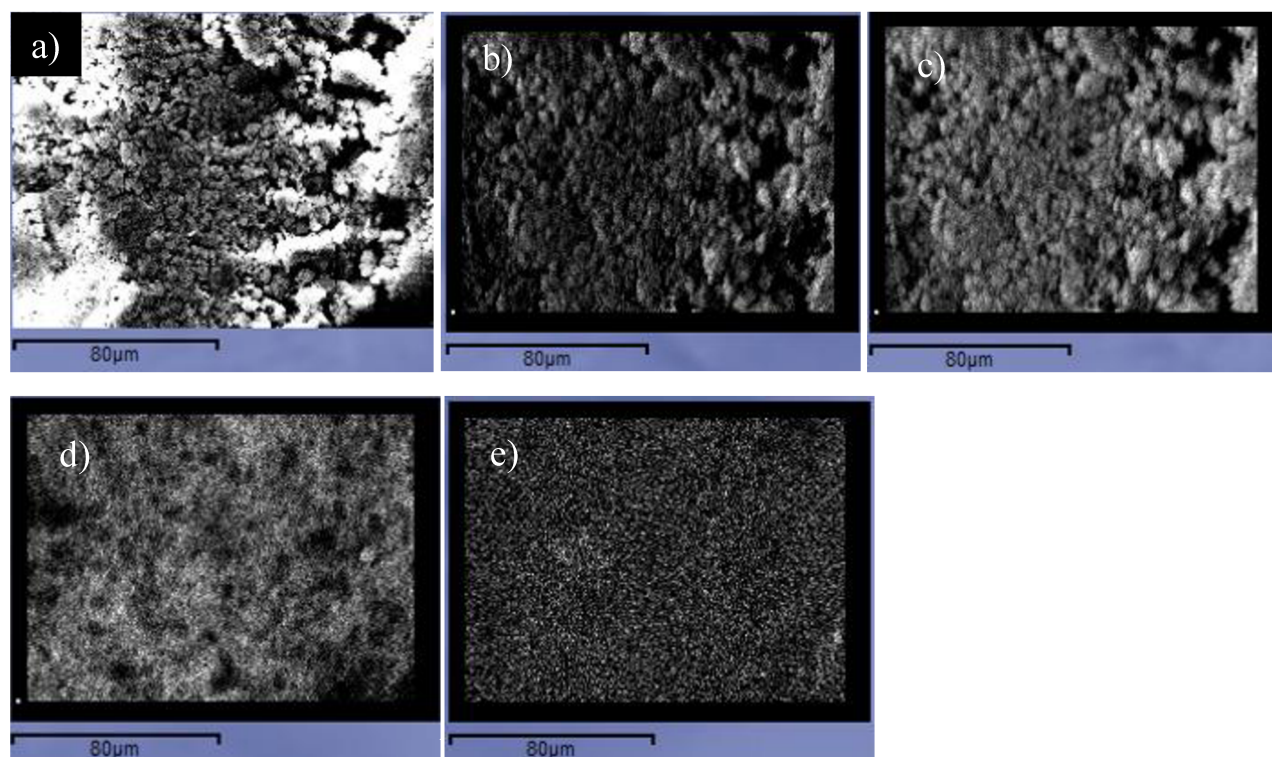


Figure S1. a) SEM image and EDX mapping of b) N, c) C, d) S and e) Ag on the surface of *SH-gC₃N₄/Ag_{1%}*

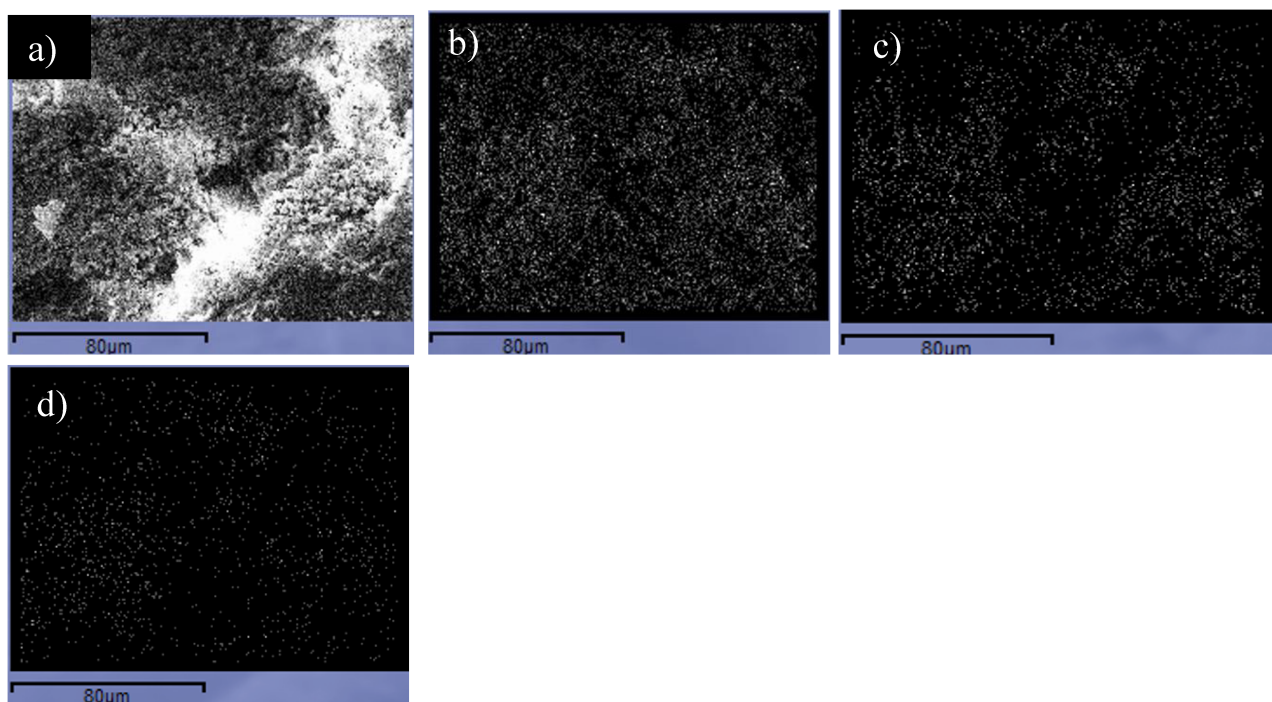


Figure S2. a) SEM image and EDX maps of b) C, c) N and d) Ag on the surface of $\text{gC}_3\text{N}_4/\text{Ag}_{1\%}$

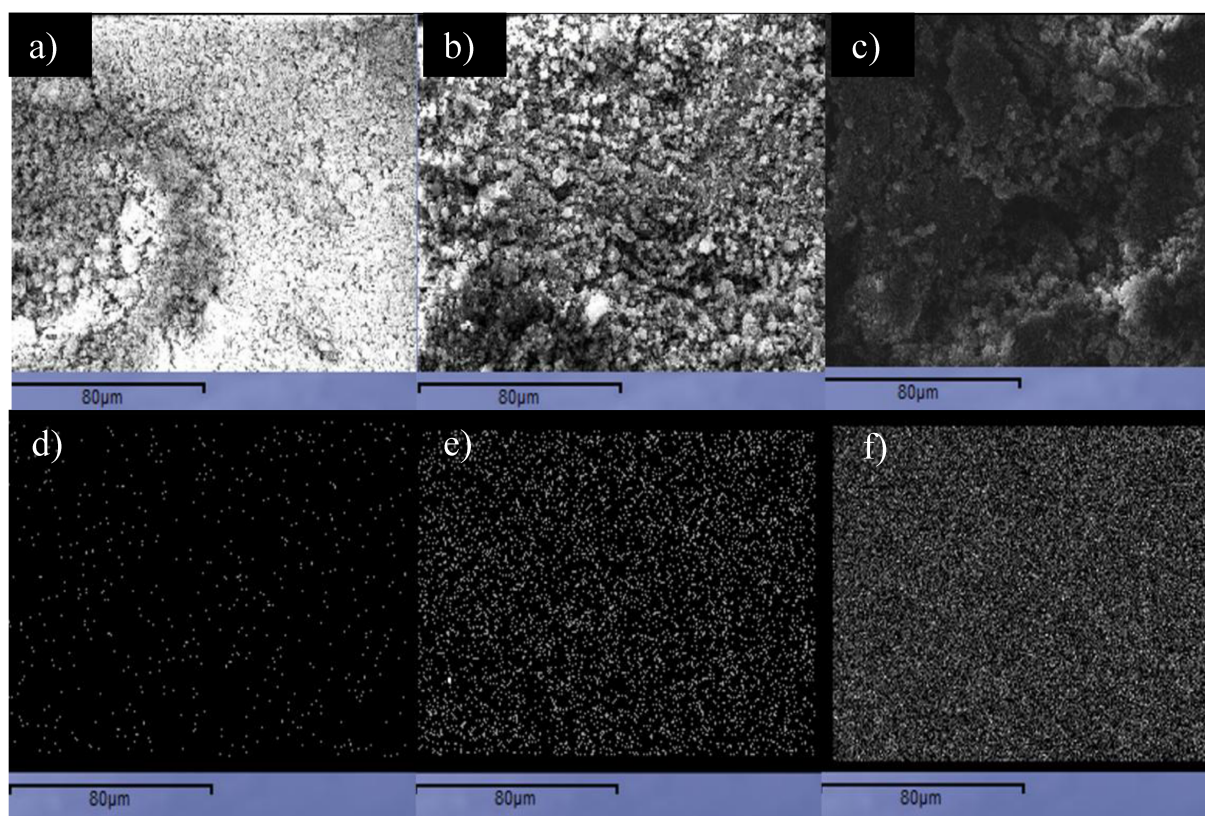


Figure S3. SEM-EDX images of $\text{gC}_3\text{N}_4(\text{T})/\text{Ag}_{0.1\%}$: the top row shows SEM images, respectively, of $T = 500$ (a), 525 (b) and 550 (c). The bottom row shows EDX Ag maps of $T = 500$ (d), 525 (e) and 550 (f)

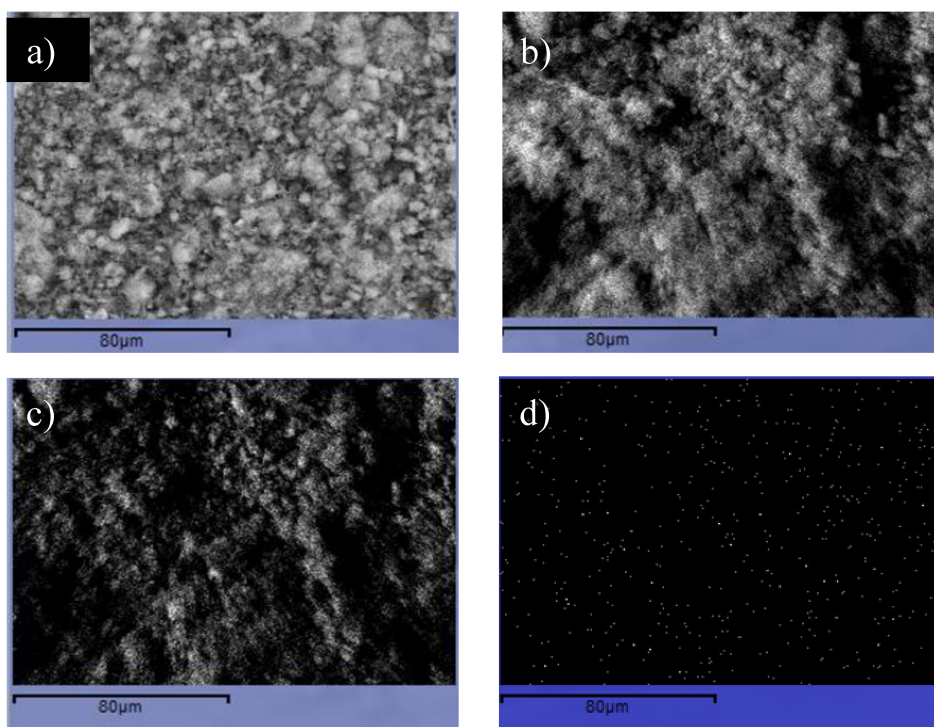


Figure S4. a) SEM image of g-C₃N₄(525)/Au nanospheres_{0.1%} and EDX mapping of b) C, c) N and d) Au on its surface.

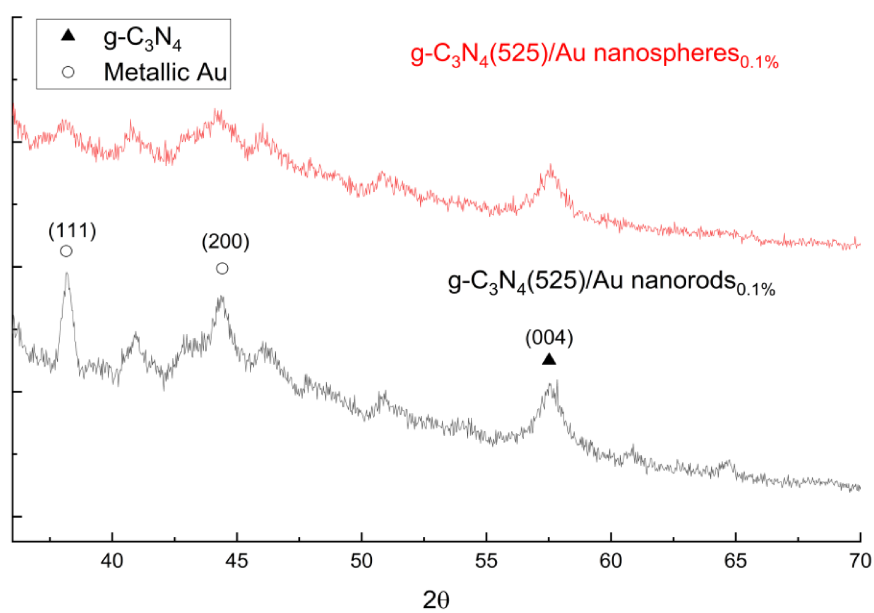


Figure S5. Enlarged view of the XRD patterns of the g-C₃N₄(525)/Au_{0.1%} system

Experimental Section

Sample synthesis and characterization

g-C₃N₄ and SH- g-C₃N₄ nanosheets

g-C₃N₄ nanosheets have been synthesized starting from the bulk form (bulk g-C₃N₄). Dicyandiamine DCD (NH₂C(=NH)NHCN, Aldrich, 99%) is polymerized under N₂ flux: the alumina boat containing densely packed DCD is positioned in a quartz tube, filled with nitrogen, and heated up in a tubular oven (4 °C min⁻¹) to the selected temperature of 550 °C, followed by an isothermal step 4 hours long and finally cooled to room temperature (6 °C min⁻¹).

To produce thermally exfoliated nanosheets, 1 gm of finely ground bulk g-C₃N₄ was placed in an alumina boat (20 mL), spread to cover homogeneously the bottom, and heated (5 °C min⁻¹) in a tubular oven under air until the desired temperature was reached. The boat was left at the desired temperature for 2 h and then cooled at room temperature (6 °C min⁻¹).

The liquid exfoliated catalyst (nanosheets) was prepared by dispersing the bulk form in a 1:1 vol% solution of ethanol and distilled water and then sonicating the mixture for 4 hours. The obtained dispersion is then centrifugated at 6000 rpm and washed with distilled water. Finally, it's dried at 60°C for 12 hours.

The thiol-group functionalization of the nanosheets (SH-gC₃N₄) was carried on by dispersing 0.2g of g-C₃N₄ nanosheets in 50 mL of deionized water containing 0.1 wt% of SDS (sodium dodecyl sulfate). In a second solution maintained under stirring at 5°C (through an ice-water bath) and containing 50 mL of deionized water, 70 mg of 4-ATP (4-aminothiophenol) and 200 mg of NaNO₂ are added 3 mL of cold HCl. This second solution is added to the dispersed g-C₃N₄ and the mixture is left stirring at ambient temperature for 4 hours. The obtained powder is centrifugated 3-4 times at 6000 rpm with deionized water and re-dispersed in DMF to completely remove SDS excess, and then washed again with de-ionized water on a paper filter.

Ag and Au nanoparticles

A three-necked flask containing 44 mL of deionized water, 5 mL of sodium citrate 50 mM and 1 mL of tannic acid 50 mM, is heated under reflux in a heating mantle while the solution is stirred. When the temperature reaches 92°C, 1 mL of silver nitrate solution is rapidly added to the flask and the rapid formation of the dark yellow **Ag NPs** solution can be observed. After a couple of seconds, the

flask is removed from the mantle and cooled at ambient temperature. The obtained solution is centrifugated at 8000 rpm for 20 minutes, and then the supernatant liquid is removed; the NPs are re-dispersed in Na_3Cit 2 mM until the volume reached is equal to the pre-centrifugation one. The process is repeated until the supernatant liquid is colourless, therefore until the complete removal of tannic acid.

The **Au nanospheres** are prepared by diluting 87 μL of HAuCl_4 1.44 M in 500 mL of twice-distilled water and the obtained solution is heated until the boiling point is reached under stirring. Separately, 0.1292g of sodium citrate trihydrate are dissolved in 25 mL of water and heated until boiling. This solution is quickly added to the first one: the obtained solution is stirred for 2.5 hours after turning off the heat, to obtained a red/pink solution.

The **Au nanorods** are prepared starting by preparing *seed* particles: in a thermo-controlled water bath (between 27 and 30°C), 25 μL of HAuCl_4 50 mM are added to 4.7 mL of CTAB 0.1M (cetrimonium bromide); the obtained solution is stirred slowly for 5 minutes, and then 300 μL of NaBH_4 10 mM are quickly added under vigorous agitation. The seed thus obtained are used to prepared the single crystal Au nanorods: still in a thermo-controlled water bath (between 27 and 30°C), 190 μL of HCl 1M and 100 μL of HAuCl_4 50 mM are added to 10 mL of CTAB 0.1 M. The obtained solution is stirred for 5 minutes, and then 60 μL of AgNO_3 10 MM are added to the solution under slow stirring, to obtain a final concentration of 6 μM . 100 μL of ascorbic acid 100 mM are added to this growth solution, that becomes colourless. Finally, 24 μL of seed@CTAB are added to the growth solution, stirred for 2h at 30°C to obtain a dark blue solution.

NPs decoration of g- C_3N_4 nanosheets

100 mg of g- C_3N_4 nanosheets are dispersed in the metallic NPs solution (the precise volume depends of the desired wt% for the final composite), whose concentration is measured by DLS and Absorption measurements. The obtained dispersion is covered and sonicated for 10 minutes and then is stirred at ambient temperature until complete evaporation of the liquid. Once dried, the recovered powder is washed in deionized water and dried on a paper filter at ambient T overnight.

Characterization

The crystal structure of the samples has been characterized by a Bruker D2 θ - θ diffractometer equipped with a Cu X-ray tube (Cu $\text{K}\alpha$, $\lambda = 1.5418 \text{ \AA}$) and a linear position sensitive detector, depositing ~ 50 mg of the powders in a Si zero-background sample-holder and acquiring the measurements in the 10-80° 2θ range, with steps of 0.02° and a time per step of 2 s. Literature

information were used for assigning space group, by visually comparing peaks positions with the characteristic reflections of the characterized compounds. The particle size and the particle concentration are determined through MADLS spectra with *ZetaSizer Ultra*. Microstructural characterization of the samples was made using a high-resolution scanning electron microscope (SEM, ZEISS-EVO 10) operated at 25 kV.

Photocatalytic Water-Splitting experiments and Hydrogen determination

Hydrogen evolution experiments took place in Pyrex glass containers (25 mL) containing 20 mL of an aqueous solution 10 % (v/v) triethanolamine (TEOA, Aldrich, $\geq 99\%$), where TEOA plays the role of sacrificial agent, and 20 mg of the photocatalyst (1 g catalyst/L solution). Oxygen was removed by Nitrogen bubbling for 20 minutes, during which the reactors stand in a ultrasound bath. For the experiments carried on in presence of 0.1% of Pt, 20 μL of a 0.005 M H_2PtCl_6 solution (hexachloroplatinic acid hydrate, 38 % Pt basis, Sigma Aldrich) as the Pt co-catalyst precursor (photo-deposited in situ on the catalyst during irradiation) was added to the suspension after 18 minutes of bubbling and sonicating and then left degassing for 2 additional minutes. The photoreactors were sealed using sleeve stopper septa. Irradiation was performed under simulated solar light (1500 W Xenon lamp, 300-800 nm) using a Solar Box 1500e (CO.FO.ME.GRA S.r.l.) at 500 W/m^2 for 4 hours. The headspace evolved gas was quantified by gas chromatography (using a molecular sieve column with a length of 30 m, an internal diameter of 0.53 mm, and a film thickness of 50 μm), coupled to a thermal conductivity detector (GC-TCD). 250 μL of gas drawn up from the reactor headspace and injected in the Gas Chromatographer. The H_2 evolution is expressed as $\mu\text{mol g}^{-1} \text{ h}^{-1}$.

The co-author Giulia Giovilli, author of the present Ph.D. work, supervised the synthesis and characterization of the heterojunctions and the quantification of photocatalytic H₂ produced.

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Chapter 4

g-C₃N₄/Bi₂MO₆ (M = Mo, W, Mo_{1-x}W_x) Heterojunctions for Solar-Driven Photocatalytic Nitrogen and Hydrogen Production

Giulia Giovilli^a, Francesca Merlo^a, Marco Moroni^a, Antonella Profumo^a and Lorenzo Malavasi^a

^a Department of Chemistry and INSTM, University of Pavia, Via Taramelli 16, Pavia, 27100, Italy

Abstract

Graphitic carbon nitride (g-C₃N₄) nanosheets, synthesized by thermal exfoliation of bulk g-C₃N₄, and Bi₂MO₆ (M = Mo, W, Mo_{1-x}W_x) compounds, made through a solvothermal synthesis followed by heat treatment, were coupled in heterojunctions with varying wt%, W-doping and crystallinity. These heterojunctions were then employed in solar-driven nitrogen fixation and hydrogen evolution: while the composite show a synergy during photocatalytic nitrogen fixation, pure g-C₃N₄ remains the best performing photocatalyst for solar-driven water-splitting. The best performing heterojunction for both NH₃ and H₂ production is amorphous Bi₂MoO₆ (2.5%)/g-C₃N₄ (97.5%): it produces 3 times the NH₃ yield of pure g-C₃N₄ (9 vs 3 μmol g⁻¹ h⁻¹) and it reaches a slightly higher yield of H₂ (145 vs 143 μmol g⁻¹ h⁻¹). Comparing Bi₂Mo_{1-x}W_xO₆(10%)/g-C₃N₄(90%) and Bi₂Mo_{1-x}W_xO₆(5%)/g-C₃N₄(95%) hydrogen production rates, W doping introduces lattice distortions that are successful in enhancing PHE: for Bi₂Mo_{1-x}W_xO₆(10%), every heterojunction is better performing than end-members, with x = 0.45 being the best performing (~ 90 μmol g⁻¹ h⁻¹, more than double the H₂ production rate of end-members); for Bi₂Mo_{1-x}W_xO₆(5%), the hydrogen production decreases with the increase of x, except for x = 0.75, who reaches ~ 130 μmol g⁻¹ h⁻¹ (nearly as high as BMO(5%)’s hydrogen production).

1. Introduction

The most abundant renewable energy source is solar energy: it can be harvested with a carbon foot-print as low as 20-50 g CO₂e kWh⁻¹ and it can be used in solar fuel technologies to synthesize value-added molecules that can be used as renewable fuel, like hydrogen, or as chemical feedstock, like ammonia.^[1] Implementing these technologies open up an alternative path toward less carbon-heavy and energy-intensive industrial processes and also remedies the intermittence of renewable energy sources by storing it in the form of chemical fuel.

Solar fuel technologies encompass a wide array of reactions and products, that, as of now, heavily rely on the use of fossil fuels. An example of this is hydrogen production: hydrogen is one of the most important secondary energy sources and has been strongly researched as a possible substitute for traditional fossil fuels, because – in addition to its high energy density (120-140 MJ/kg) – its combustion is a carbon-free process and it can also be produced without any carbon emission (*green hydrogen*) through the use of renewable energy sources^[2]. Presently, hydrogen is produced almost entirely from fossil fuels, with the most employed process being methane-steam reforming, but several different approaches to the production of green hydrogen exists and are actively being researched right now^[3,4].

Another example is ammonia production: one of the most invaluable chemical compound on the global market (88% of the 180 million ton of ammonia produced yearly are used in the production of 60% of nitrogen-rich fertilizers), ammonia is also a good choice as an energy storage medium or as high-density liquid fuel because it has high energy density (3 kW h kg⁻¹), high hydrogen content (17.7 wt%) and it's easy to store and transport.^[5] Industrially, the most used method of production is still the Haber-Bosch process: because of the harsh conditions needed for the reaction to happen (high temperature and pressure) and the natural gas used as a hydrogen source, it accounts for 2% of the global energy expended annually and releases around 300 million metric tons of CO₂. To truly make

ammonia a viable solar fuel, it's imperative to further research and develop green alternatives to the Haber-Bosch process.

Both green H_2 and NH_3 can be produced by solar-driven (or visible-light-driven, VLD) photocatalysis, through water splitting (or photocatalytic hydrogen evolution, PHE) and photocatalytic nitrogen fixation (PNF). Both reactions are carried out in an heterogenous system under mild conditions, where the solid photocatalyst is dispersed in water: the photocatalytic material is usually a semiconductor with a band gap chosen to maximize the light absorbed and whose energy bands align well with the redox potential of the chemical reaction. Absorbed photons excite electrons that move from the valence band to the conduction band of the material, leaving holes. After this charge separation, charge carriers will migrate toward the surface of the catalyst, resulting in the reduction of electron acceptors and the oxidation of electron donors.^[1]

The biggest challenges to these photocatalytic processes are: i) short charge-carriers lifetime, ii) reduced light absorption, iii) low number of easy-to-reach sites where reagents can be absorbed and activated, iv) limited surface reactivity and, especially for PNF, v) the competing hydrogen evolution reaction. Most photocatalytic systems still rely on wide band gap semiconductors like TiO_2 , which absorbs only deep blue and violet photons, that makes up only 5% of visible light. It's necessary to develop photocatalytic materials able to better separate charge-carriers and ease their migration toward active sites on the material. They also need to have an energy band structure that enhances light absorption and that matches well the desired redox reactions potential, and enough superficial sites available for reagent molecules to occupy.^[6]

Using a VLD photocatalyst is a great alternative to enhance light absorption: Bi_2MoO_6 and Bi_2WO_6 , having attracted the attention of many researchers for their photocatalytic applications, are examples of these materials.^[7–10]

Bi_2MO_6 (with $M = W, Mo$) are the simplest, most-popular oxides in the complex Aurivillius series $(Bi_2O_2)^{2+} (A_{n-1}B_nO_{3n-1})^{2-}$, where A sites are usually occupied by mono-, di- or tri-valent

metal ions, and B sites are occupied by penta- or hexa-valent transition metals. The n number in this compositional formula indicates the number of perovskite layers comprised of BO_6 octahedrons ($n = 1-8$).^[11] $[\text{Bi}_2\text{O}_2]^{2+}$ sheets and $[\text{MO}_4]^{2-}$ perovskite-type layers are interwoven into a layered structure that crystallizes into an orthorhombic systems: strong covalent bonds exist within layers, Mo–O bond length (~ 1.76 Å) in Bi_2MoO_6 exceeds the W–O bond length (~ 1.72 Å) in Bi_2WO_6 , while interlayer cohesion is governed by weak van der Waals forces. The lower bond-length of W–O depend on the higher electronegativity of W (2.36) when compared to Mo (2.16), so W tends to form more covalent bonds, leading to a contraction of the crystal structure and a reduced interplanar spacing in Bi_2WO_6 . Both Bi_2MoO_6 (BMO) and Bi_2WO_6 (BWO) are thermally stable (BMO below 500°C and BWO until $600-700^\circ\text{C}$) and chemically stable, thanks to their strong covalent bonds and stable oxidation states.^[12,13] The layered crystal structure not only provides a large specific surface area (usually $50-100\text{ m}^2\cdot\text{g}^{-1}$), which exposes more active sites but also shortens the migration distance of photogenerated charge carriers, reducing their recombination rate.^[12]

The surface of Bi_2MO_6 compounds is rich in defect sites – like oxygen vacancies, caused by the high temperature methods mostly employed to synthesize them – that trap electrons, suppress charge recombination and enhance adsorption. Surface Bi^{3+} ions adsorb and activate N_2 molecules through coordination bonds that weaken N–N triple bond, while surface O^{2-} ions donate electrons in the N_2 antibonding orbitals, lowering activation barriers.^[12]

Among the members of the Aurivillius family, Bi_2MoO_6 , Bi_2WO_6 and $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$ solid solutions are Visible-Light-Driven (VLD) n-type semiconductor photocatalyst; the hybridization between Bi 6s and O 2p orbitals contribute predominantly to the valence band (VB), while the conduction band (CB) is predominantly composed by M nd ($n=4, 5$) orbitals, resulting in a band gap ranging from 2.5 to 2.9 eV.^[6,12,14] This band configuration, paired with the stack-layered structure and its internal electrical field, is also conducive to photocarriers separation and their migration toward

active sites, with holes being mostly localized on Bi and O atoms, while electrons move toward the transition metal M.

Bi_2MO_6 band-gaps are highly tunable through morphological, structural and chemical modifications; BMO and BWO possess E_{VB} and E_{CB} conducive to carry on both the nitrogen reductive reaction (NRR, -0.28 V vs NHE) and the oxygen evolution reaction (OER, +1.23 V vs NHE).^[6,12,13,15–19] When irradiated with visible light, photogenerated electrons in the CB can quickly migrate toward surface sites where they effectively activate the inert $\text{N}\equiv\text{N}$ bond in nitrogen molecules, while photogenerated holes remaining in the VB are provided with enough oxidizing power for water splitting. Because CB's potential matches well with NRR potential, BMO and BWO show an ammonia selectivity over 90%, avoiding to a large extent the competitive hydrogen evolution reaction (HER, 0 V vs NHE)^[20]; in addition Bi-based matrices tend to be highly hydrophobic, forming instead strong interactions with N_2 molecules.^[13]

In addition to the wide light absorption range and tunable band gap, these materials are non-toxic (despite Bi being a heavy metal, it's biocompatible because it gets excreted through urine), highly stable, easy to synthesize and precursor materials are pretty cost-effective.^[12] Nevertheless, pure Bi_2MO_6 's photocatalytic activity still suffer due to poor visible-light utilization, low specific-surface area, low carrier mobility, high carrier-recombination rate.^[14]

There are many possible methods that can be employed to enhance the photocatalytic activity of these semiconductors. In this work, we employed: i) structural modification (crystalline vs amorphous compounds), ii) doping ($\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$ solid solution series) and iii) construction of heterojunctions with another semiconductor, graphitic carbon nitride g- C_3N_4 .

g- C_3N_4 is a unique non-metallic copolymer n-type semiconductor material made of stacked 2D C-N layers similar to graphene. It absorbs in the visible light range ($E_g \sim 2.7$ eV) and the band position is suitable for both PHE and PNF reactions. Bulk g- C_3N_4 synthesis is cheap and easy, and a subsequent heat treatment with variable temperature and duration can be used to synthesize g- C_3N_4

nanosheets, with a higher surface area, reduced thickness and thus a reduced migration distance to the photocatalyst surface for the photogenerated carriers, and a higher number of surface defects (mostly nitrogen vacancies) that adsorb and activate reagent molecules.^[15,16,18]

The aim of this work was the synthesis of Bi_2MoO_6 , Bi_2WO_6 and $Bi_2Mo_{1-x}W_xO_6$ solid solution series in both crystalline and amorphous form. These semiconductors were then used to synthesize composite with g-C₃N₄ nanosheets in various ratio and then their photocatalytic activity was studied for both photocatalytic nitrogen fixation and photocatalytic water-splitting to determine how much variables like component wt%, value of x (W-doping) in $Bi_2Mo_{1-x}W_xO_6$ solid solutions and type of material affect ammonia and hydrogen production yields.

2. Results and Discussion

The amorphous and crystalline $Bi_2Mo_{1-x}W_xO_6$ series has been synthesized according to the experimental procedure reported in the Supporting Information (SI) which is schematically represented in Figure 1. According to the different molar ratios of W and Mo used during the synthesis, we prepared six $Bi_2Mo_{1-x}W_xO_6$ compounds with $x = 0.15, 0.3, 0.45, 0.60, 0.75, 0.9$, plus the two end-members Bi_2MoO_6 (BMO) and Bi_2WO_6 (BWO). The procedure adopted to obtain these series of compounds is simple and makes use of cheap precursors.

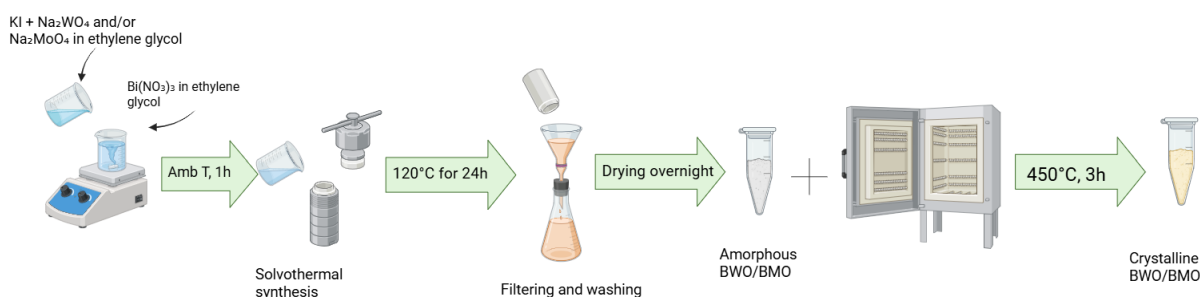


Figure 1. Schematic illustration of the synthetic procedure to obtain the $Bi_2Mo_{1-x}W_xO_6$ series

The X-ray diffraction (XRD) patterns of the different solid solutions are reported in figure 2a and 2b for the amorphous and crystalline series respectively, while figure 2c and 2d shows the two crystalline end-members compared with calculated reflections.

The good match between the experimental and calculated patterns confirm that both samples present an orthorhombic crystal structure (space group $Pca2_1$), coherently with what can be found in literature^[21], with no unreacted reagents or secondary products present in the final sample. All samples belonging to the $Bi_2Mo_{1-x}W_xO_6$ series also present the same orthorhombic crystal structure and a gradual transformation of the diffraction pattern with the increase of the quantity of W in the compound can be seen for both amorphous and crystalline samples alike.

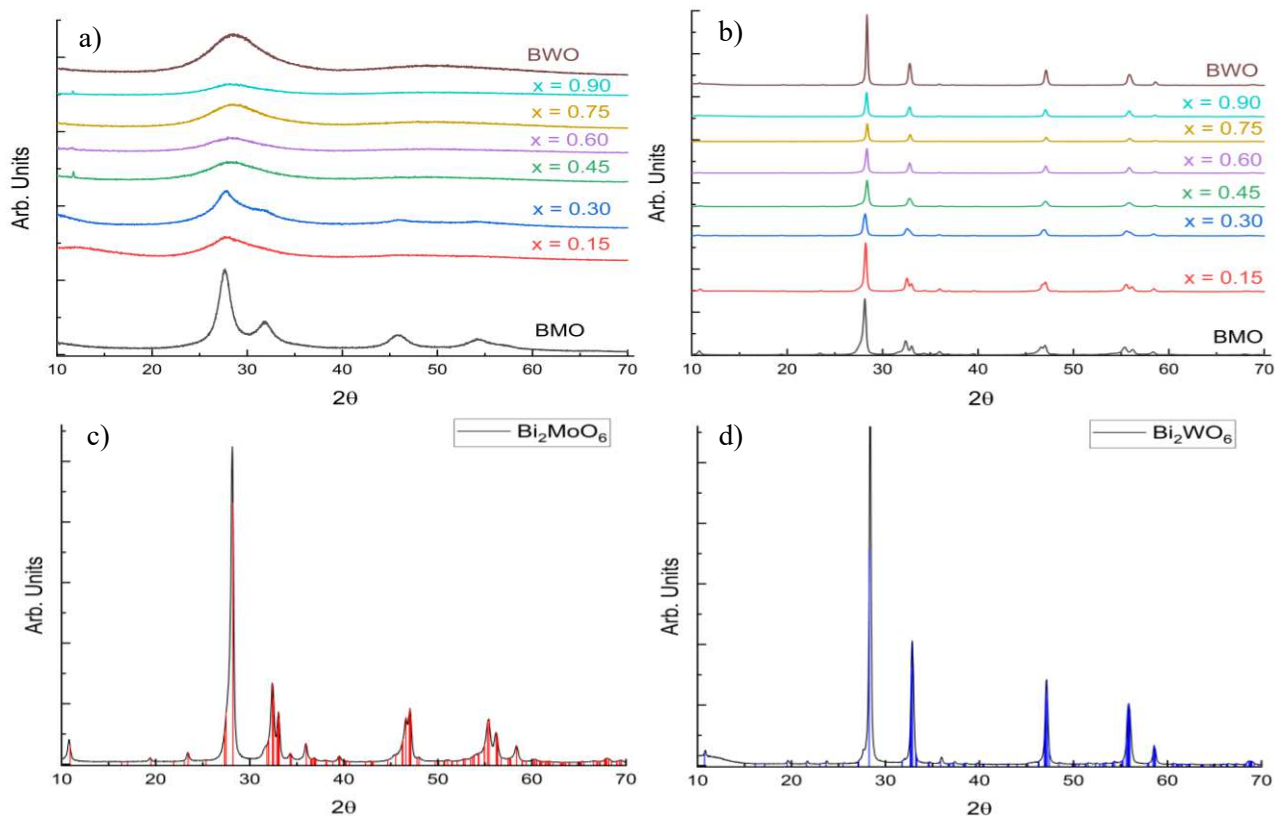


Figure 2. X-Ray Diffraction patterns of the a) amorphous $Bi_2Mo_{1-x}W_xO_6$ series and b) crystalline $Bi_2Mo_{1-x}W_xO_6$ series, c) Bi_2MoO_6 XRD pattern against calculated pattern and d) Bi_2WO_6 XRD pattern against calculated pattern

Experimental data were also refined through Rietveld refinement to determine lattice parameters a, b and c , and *lattice volume*. The diffraction patterns of Bi_2MoO_6 and Bi_2WO_6 were found to be similar to the JCPDS card no. 72-1574, ($a = 5.506 \text{ \AA}$, $b = 16.2260 \text{ \AA}$, $c = 5.487 \text{ \AA}$) and JCPDS Card no. 390256, ($a = 5.456 \text{ \AA}$, $b = 16.445 \text{ \AA}$, $c = 5.444 \text{ \AA}$), respectively.^[22] In accordance with previous findings, these Aurivillius compounds (Bi_2MO_6 with $M=Mo, W$) depart from Vegard's Law^[11]: deviations can be seen both in the lattice parameters and in the volume, probably due to lattice distortion generated by W-doping induced contraction.^[22]

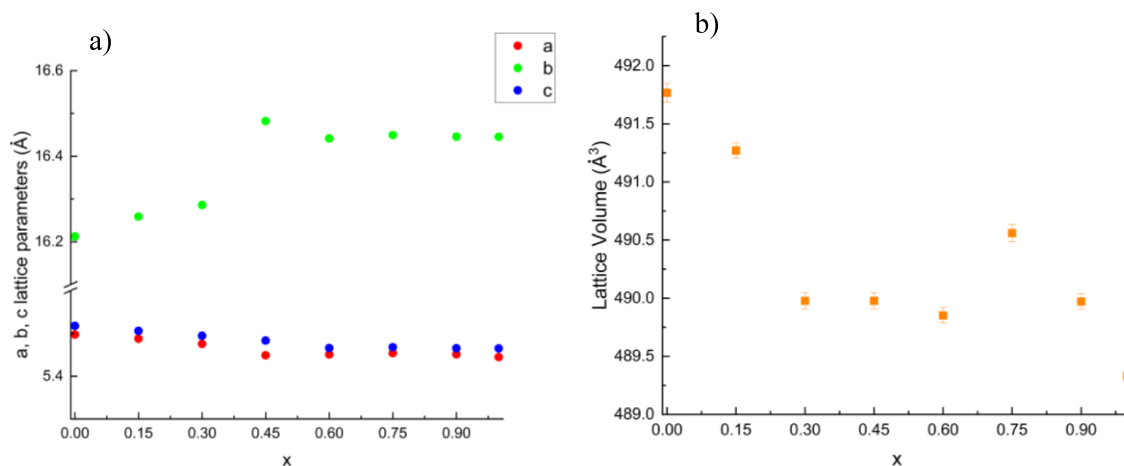


Figure 3. Trend of a) a, b and c lattice parameters, b) cell volume for the samples of the $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$ solid solution as a function of x .

The morphological properties of the samples have been studied by scanning electron microscopy (SEM) and results are reported in figure S1. We reported the images of both amorphous and crystalline Bi_2MoO_6 (S1a and S1b) and Bi_2WO_6 (S1c and S1d): all samples show micro-sized agglomerates of spherical particles, the only difference being that crystalline Bi_2MoO_6 particles present the flake-type microstructure common for Aurivillius-type materials while crystalline Bi_2WO_6 particles look more jagged than their amorphous counterpart.^[23,24]

UV-Vis absorption spectra and band gaps – calculated using Tauc plots (figure S3) – are reported in Figure 4. The indirect band gap of c-BMO is around 2.55 eV and the one of c-BWO is around 2.82 eV, in agreement with previously recorded values found in literature. The indirect band gap of a-BMO and a-BWO are higher (2.66 and 2.96 respectively), but still in agreement with the band-gap range. The intermediate compounds show very slight variation of the band gap energy, with the majority of them having nearly the same band gap as BMO: the only outlier is crystalline $\text{Bi}_2\text{Mo}_{0.25}\text{W}_{0.75}\text{O}_6$ with a band gap of 2.64 eV. While the expected trend for solid solutions would be for the band gap to increase linearly^[14], in the case of $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$, the band gaps of solid solutions with $x \leq 0.6$ remain near the value of Bi_2MoO_6 and the ones of solid solutions with $x > 0.6$ should increase with the content of W. That's true for $x = 0.75$, while $x = 0.9$ shows a dramatic drop in value (2.51 eV), even lower than Bi_2MoO_6 .

The band gaps of $Bi_2Mo_{1-x}W_xO_6$ solid solutions depend on two factors: the presence of W 5d and Mo 4d orbitals in the conduction band, and W-substitution causing lattice distortion and subsequent delocalization of excitation energy^[14], a possible explanation of why the band gap of $Bi_2Mo_{0.1}W_{0.9}O_6$ is so much lower than that of $Bi_2Mo_{0.25}W_{0.75}O_6$.

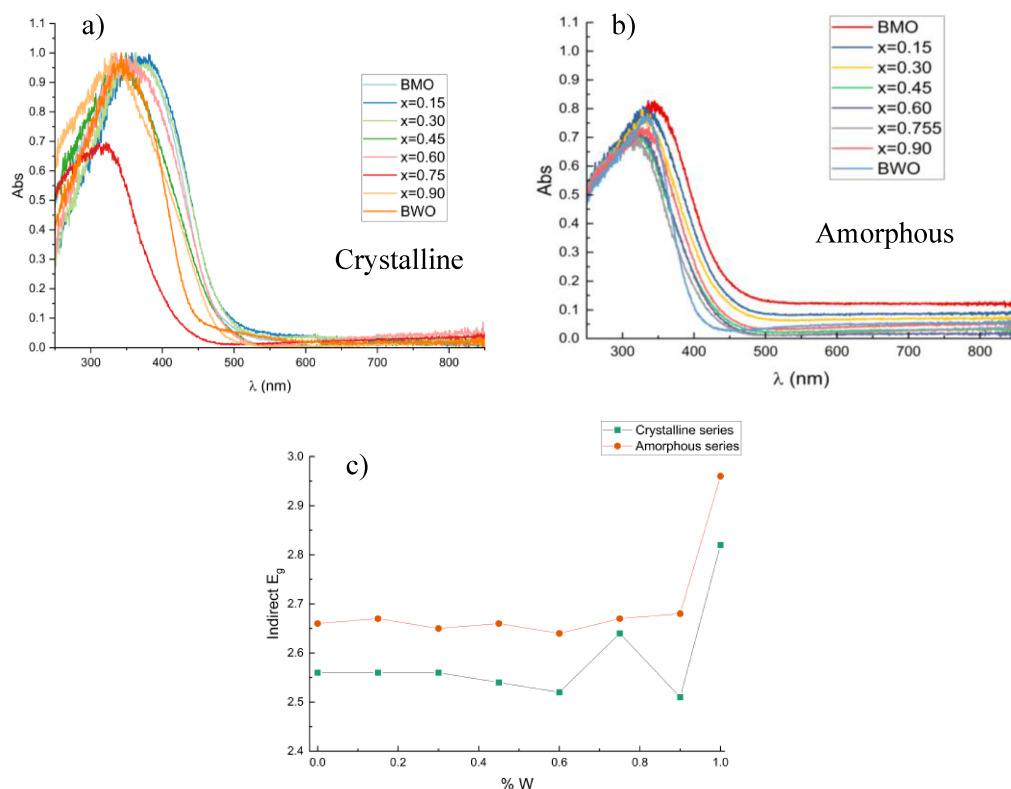


Figure 4. UV-Vis Absorption spectra of a) crystalline and b) amorphous $Bi_2Mo_{1-x}W_xO_6$ solid solutions, and c) trend of the indirect band gaps for $Bi_2Mo_{1-x}W_xO_6$ solid solutions

After synthesizing and characterizing the two solid solutions series, we decided to synthesize four sets of heterojunctions by coupling amorphous and crystalline BMO and BWO with g- C_3N_4 : the weight ratios investigated are (wt% of g- C_3N_4) 0, 80, 90, 95, 92.5 and 100. The experimental procedure can be found in the Supporting Information (SI) and it's schematically represented in Figure 5.

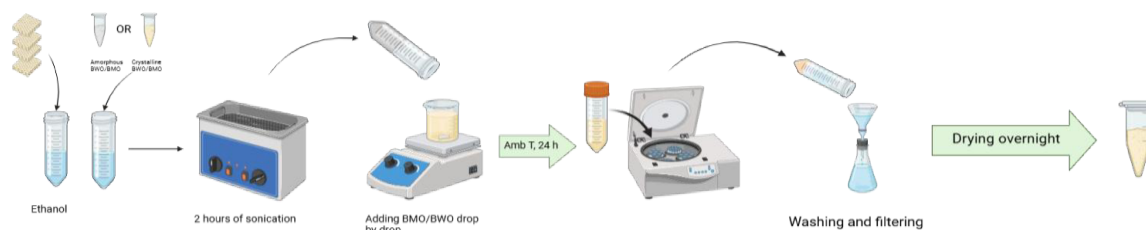


Figure 5. Schematic illustration of the synthetic procedure to obtain heterojunctions containing a- and c-BMO (or BWO) and g- C_3N_4

X-ray diffraction (XRD) patterns of the different sets of heterojunctions are reported in figure

6.

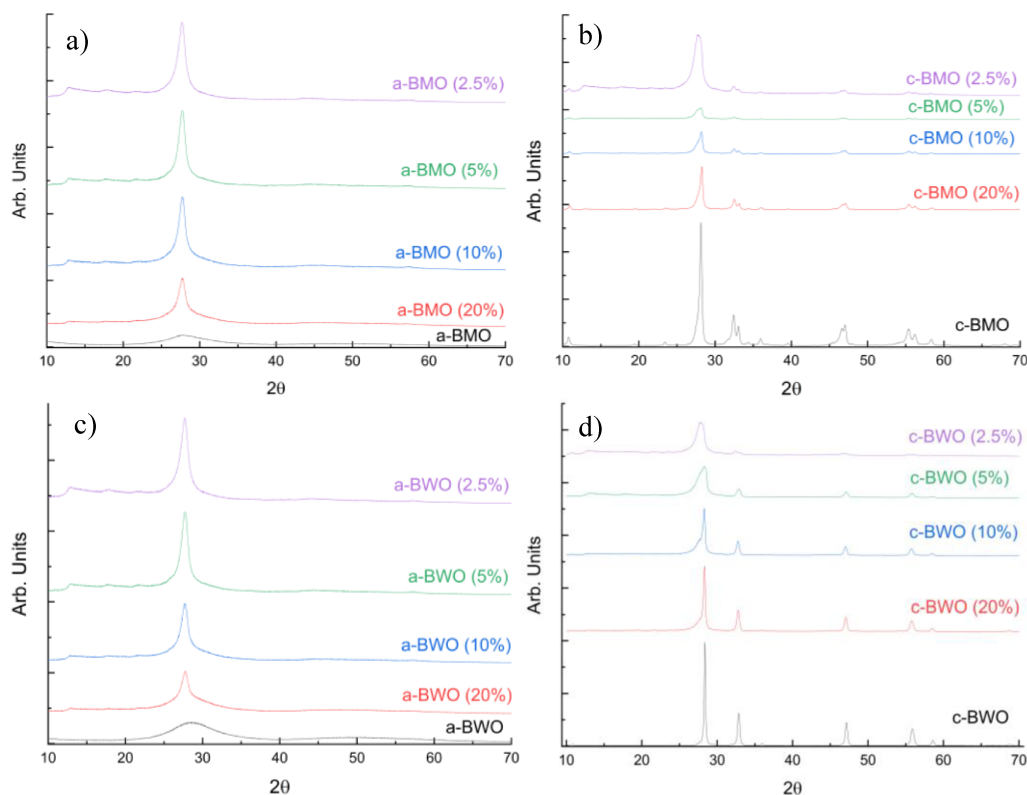


Figure 6. X-Ray Diffraction patterns of the a) amorphous $\text{Bi}_2\text{MoO}_6/\text{g-C}_3\text{N}_4$, b) crystalline $\text{Bi}_2\text{MoO}_6/\text{g-C}_3\text{N}_4$, c) amorphous $\text{Bi}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ and d) crystalline $\text{Bi}_2\text{WO}_6/\text{g-C}_3\text{N}_4$ series of heterojunctions

In figure 6a and 6c we can see that with an increased quantity of $\text{g-C}_3\text{N}_4$, the contribution to the pattern of the graphitic carbon nitride starts encompassing the amorphous Bi_2MO_6 until the quantity of the amorphous oxide is so low that heterojunction's patterns can't be told apart from pristine $\text{g-C}_3\text{N}_4$ one (figure S2). Instead, when considering c-BMO and c-BWO heterojunctions (6b and 6d), we can see that the higher scattering density of the crystalline compounds is enough for Bi_2MO_6 peaks to show up even when their wt% are very low.

UV-Vis absorption spectra are reported in figure 7: heterojunctions show sharper absorption bands, similar to Bi_2MO_6 end-members, but with a λ_{max} red-shifted toward $\text{g-C}_3\text{N}_4$. Heterojunctions also presents extended absorption tails in the visible range caused by the presence of $\text{g-C}_3\text{N}_4$, typical

for sample with low-crystallinity, as is the case for the amorphous-like structure of g-C₃N₄.^[25–27] The absorption band of compounds that are part of the a-BMO/g-CN heterojunction series is subsumed by the extended absorption tail, most probably because of the low crystallinity of BMO. The lower the quantity of a-BMO, the higher the absorption band grows in height and the more λ_{max} is shifted toward g-C₃N₄; this is true for every heterojunction, the absorption band is always red-shifted when compared with pure BMO or BWO.

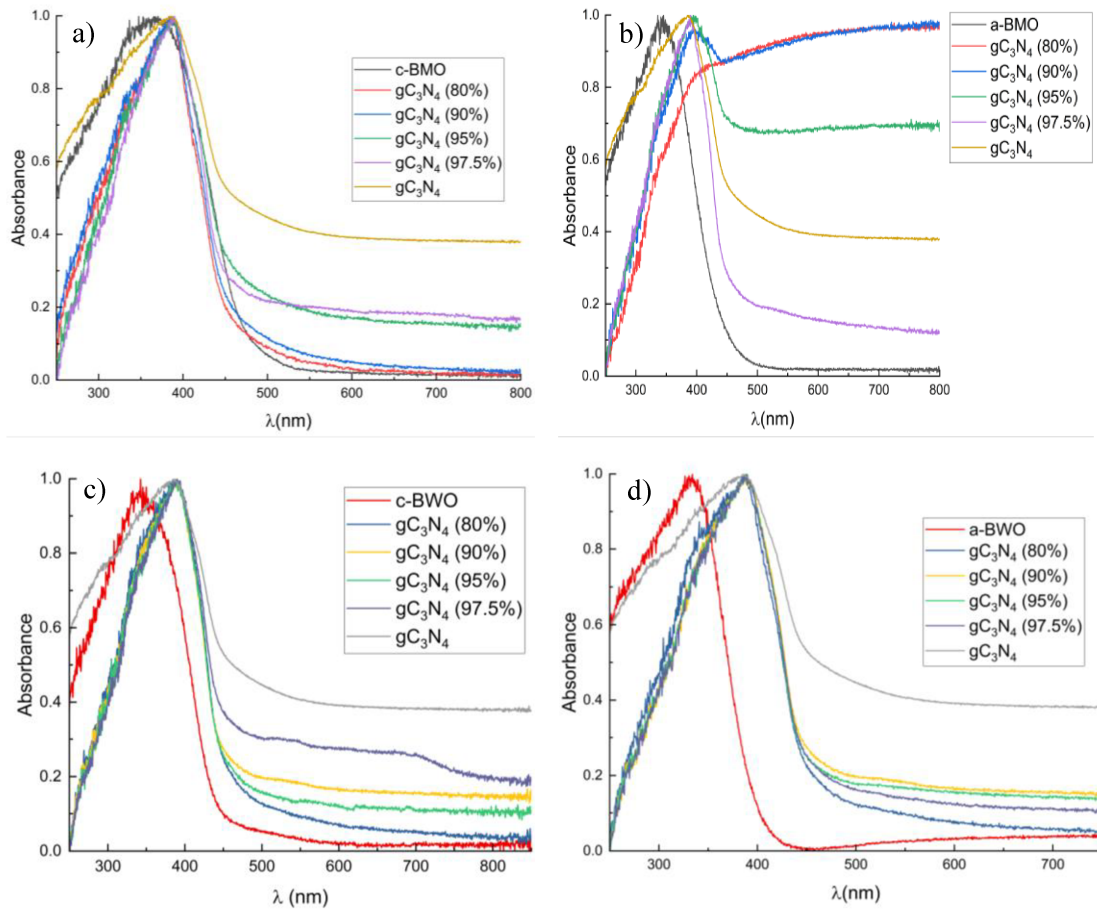


Figure 7. UV-Vis Absorption spectra of A) crystalline Bi₂MoO₆/g-C₃N₄, B) amorphous Bi₂MoO₆/g-C₃N₄, C) crystalline Bi₂WO₆/g-C₃N₄ and D) amorphous Bi₂WO₆/g-C₃N₄ series of heterojunctions

Band gaps calculated using Tauc plots (Figure S3) are shown in figure 8: either coupling Bi_2MO_6 by crystallinity or by transition metal M doesn't change the fact that heterojunctions show mirrored trends, with values much nearer those of pure $\text{g-C}_3\text{N}_4$ than the pure Aurivillius compounds, in agreement with literature.^[28]

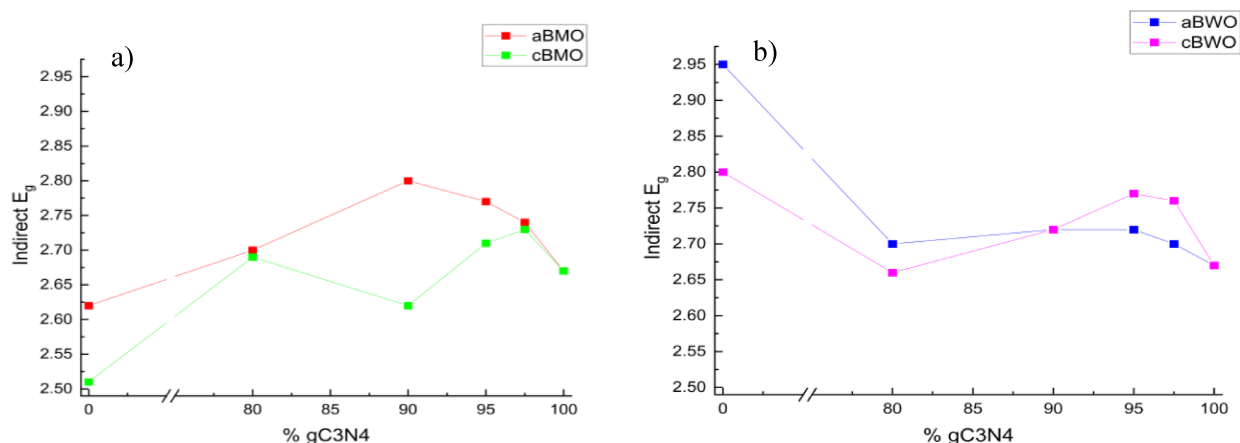


Figure 8. Indirect band gaps of A) BMO/ $\text{g-C}_3\text{N}_4$ and B) BWO/ $\text{g-C}_3\text{N}_4$ heterojunctions

A report of the results in terms of ammonia evolution rates and hydrogen evolution rate is shown in figure 9, expressed as $\mu\text{mol g}^{-1}\text{h}^{-1}$, obtained by photocatalytic experiments under simulated solar light. Experimental details are provided in the SI for the photocatalytic experiments, the ammonia and the hydrogen determination techniques: the former has been done by an ammonia ion selective electrode (ISE), which guarantees accurate detection over colorimetric methods^[29–31], and the latter by gas chromatography using a TC detector.

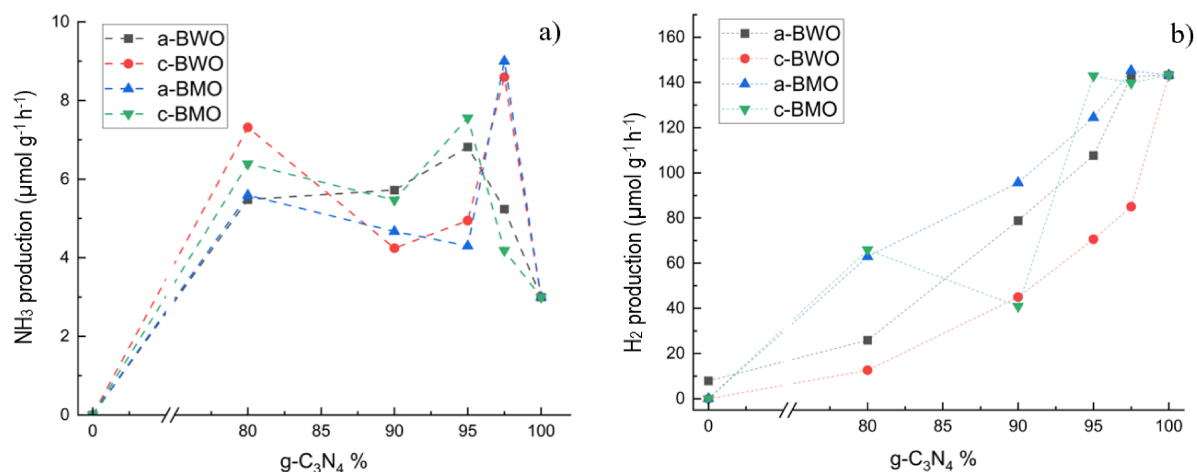


Figure 9. a) Ammonia and b) hydrogen productions as a function of $\text{g-C}_3\text{N}_4$ wt% in the composites. (simulated solar light, 500 W m^{-2})

In figure 9a, we can see that coupling these Aurivillius-type oxides with g-C₃N₄ creates a synergy: all 16 heterojunctions show a higher ammonia yield than pure crystalline and amorphous BMO and BWO (under LOQ) and pristine g-C₃N₄ (about 3 $\mu\text{mol g}^{-1}\text{h}^{-1}$). We can still recognize the same mirrored trends between the amorphous and crystalline form of the same compound: g-C₃N₄ (95%) is the best performing wt% for a-BWO/g-C₃N₄ (6.8 $\mu\text{mol g}^{-1}\text{h}^{-1}$) and c-BMO/g-C₃N₄ (7.6 $\mu\text{mol g}^{-1}\text{h}^{-1}$) heterojunctions, while g-C₃N₄ (97.5%) is the best performing wt% for the c-BWO/g-C₃N₄ (8.6 $\mu\text{mol g}^{-1}\text{h}^{-1}$) and a-BMO/g-C₃N₄ (9 $\mu\text{mol g}^{-1}\text{h}^{-1}$) heterojunctions, with these last two being the best-performing ones.

We can determine that photocatalytic nitrogen fixation is highly dependent on the characteristics of Bi₂MO₆: the same wt% produce different quantities of nitrogen depending on the transition metal M (Mo or W) and the crystallinity. Fixing either the crystallinity of the material or the transition metal vs g-C₃N₄ wt% will give the same result: the NH₃ yield production trends in such a way that a material like amorphous BMO will have opposite results when compared to amorphous BWO (fixed crystallinity) or crystalline BMO (fixed transition metal). This happens because, most of all for Bi₂MO₆ wt% under 20%, the ammonia production trends of c-BMO and a-BWO are very similar, as are the ones of a-BMO and c-BWO.

Figure S4 shows the correlation between E_g and NH₃ production for heterojunction with the same Bi₂MO₆/g-C₃N₄ ratio. For higher concentrations of Bi₂MO₆, heterojunctions perform systematically better when they have lower E_g : for Bi₂MO₆ (20%), the crystallinity has a higher impact on ammonia yields than the transition metal, because a-BMO and a-BWO have the same band gap (2.70 eV) and the same yield, while the difference between them and their crystalline counterparts (2.66 eV for c-BWO and 2.69 eV for c-BMO) is enough to enhance the photocatalytic reaction (figure S4a).

Intermediate ratios (10 and 5%) show an interesting trend: for both ratios (figure S4b and c), the best performing heterojunctions are a-BWO (2.72 eV for both 10% and 5%) and c-BMO (2.62

eV for 10% and 2.71 for 5%). Notably, for Bi_2MO_6 (10%), a-BWO and c-BWO have the same band gap, but the amorphous compound performs better (5.7 vs $4.2 \mu\text{mol g}^{-1} \text{h}^{-1}$).

Finally, the lowest concentration of Bi_2MO_6 (2.5%) show a totally opposite behaviour (figure S4d): a-BMO and c-BWO present the highest E_g (2.74 and 2.76 eV), but also the highest yields of all heterojunctions (9 and $8.6 \mu\text{mol g}^{-1} \text{h}^{-1}$).

If we consider 2.7 eV (the ideal band gap of g- C_3N_4) our centre value, we can see that heterojunctions containing c-BMO and a-BWO heterojunctions perform well when their band gap is near 2.7 eV, c-BWO heterojunctions perform well when their band gap is far from 2.7 eV, while the band gaps of a-BMO heterojunctions need to fall in an intermediate position for the material to perform well.

The hydrogen production rates seen in figure 9b show the same trends for all the heterojunctions, a linear increase with the increase of g- C_3N_4 wt%, with the best performing material being a- Bi_2MoO_6 (2.5%)/g- C_3N_4 (97.5%). Compounds containing crystalline and amorphous Bi_2MoO_6 are the best performer in the series: they show similar yields for the lower (2.5%) and highest (80%) ratios investigated, but presents differing results when considering the intermediate ratios (90 and 95%). The only outlier is the very low hydrogen yield of c-BMO (10%)-g- C_3N_4 (90%), even lower than c-BWO(10%)-g- C_3N_4 (90%).

It's clear that hydrogen yields are dependent on g- C_3N_4 wt%: the higher its quantity, the more hydrogen is produced. It's expected due to the much higher selectivity of Bi_2MO_6 materials toward ammonia evolution, but different transition metals and crystallinity still affect the photocatalytic activity of the heterojunction (figure S5).

For Bi_2MO_6 (20%), a- and c-BMO are much better performers than a- and c-BWO (figure S5a); considering that a-BMO and a-BWO have the same band-gap energy (2.70 eV), we can assert that the electronic structure of BMO is a better match for g- C_3N_4 than BWO.

In comparison, c-BWO heterojunctions are consistently the worst performers, whatever their band-gaps are (from 2.66 to 2.76 eV): only for $\text{Bi}_2\text{MO}_6(10\%)$, c-BWO(10%) (2.72 eV) shows a slightly better yield than c-BMO (10%), who has a much lower band-gap of 2.62 eV (figure S5b). It's probable that the narrowing of c-BMO's E_g is enough to move the energy levels out of their optimal positions; this increases the rate at which charge carriers recombine, decreasing significantly the hydrogen produced when compared to the expected yield. The amorphous structure of a-BWO (10%) significantly improves hydrogen production when compared with c-BWO (10%), even if they share the same E_g (2.72 eV).

The smaller sizes of a-BWO agglomerates provide a higher surface area and thus a better superficial contact between the Aurivillius material and $\text{g-C}_3\text{N}_4$. In addition, its intrinsically disordered nature results in a substantial number of "dangling bonds" and structural defects, that function as additional active sites and modify electron distribution.^[32,33]

The smaller particle size and the amorphous structure are also the probable reasons why a-BMO heterojunctions tend to perform well at every ratio, even if E_g values fluctuate from low (2.7 eV) to high (2.8 eV).

Considering the lower Bi_2MO_6 ratios (5% and 2.5%), both amorphous compounds and c-BMO show high hydrogen production, very near to pure $\text{g-C}_3\text{N}_4$ hydrogen yield. C-BMO (5%) and c-BMO (2.5%) show very similar yields, the slight decrease in production is correlated to the decrease in quantity of c-BMO. The hydrogen production of a-BMO and a-BWO, instead, increases with the decrease in quantity from 5% to 2.5%. It's clear that the photocatalytic behaviour is dominated by $\text{g-C}_3\text{N}_4$'s contribution: a-BMO, a-BWO and c-BMO's band gaps are all different (ranging from 2.70 to 2.77 eV), but they produce similar quantities of hydrogen, while c-BWO's production is approximately halved.

In conclusion, c-BMO heterojunctions perform well when their E_g is near 2.7 eV, c-BWO are always bad performers, a-BMO always perform well and a-BWO perform well only in lower quantities.

We decided to further investigate the photocatalytic behaviour in hydrogen production of these heterojunctions by synthesizing, using the same procedure, $g\text{-C}_3\text{N}_4(90\%)/\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6(10\%)$ composites with $x = 0.15, 0.3, 0.45, 0.60, 0.75, 0.9$. For comparison, we also decided to synthesize the $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6(5\%)/g\text{-C}_3\text{N}_4(95\%)$ series.

X-ray diffraction (XRD) patterns of the two different sets of heterojunctions are reported in figure 10. For both series we can see the characteristic structure of the solid solutions even in low quantities, and, as for the pure solid solutions, it's easy to see the gradual pattern transformation with the increased W-doping.

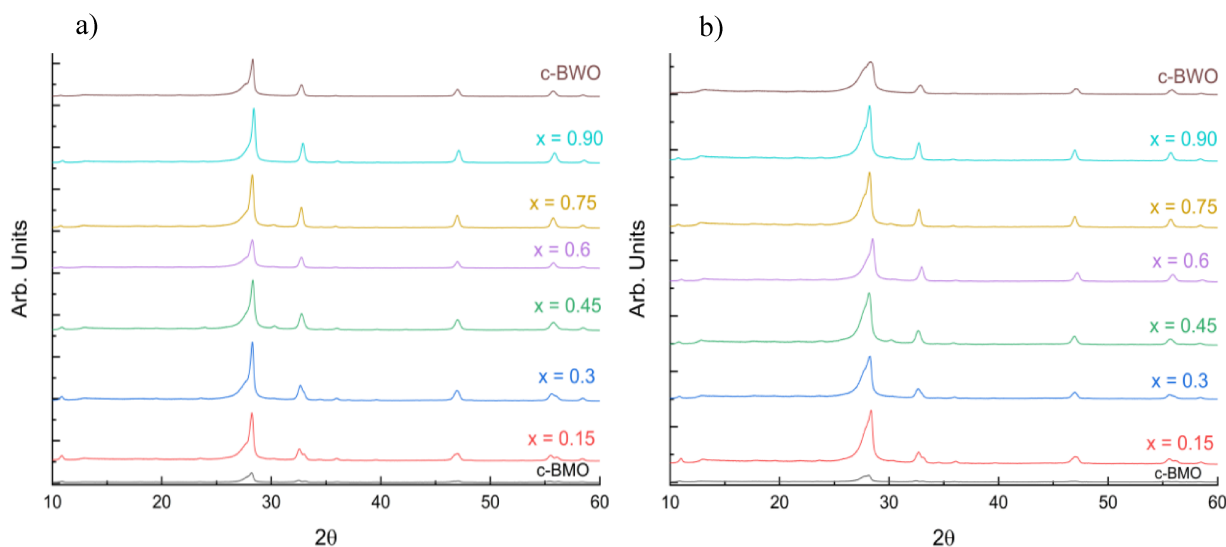


Figure 10. X-Ray Diffraction patterns of the a) crystalline $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6(10\%)/g\text{-C}_3\text{N}_4(90\%)$ and b) crystalline $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6(5\%)/g\text{-C}_3\text{N}_4(95\%)$ series of heterojunctions

Uv-Vis Absorption spectra for both heterojunction series, $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6(10\%)/g\text{-C}_3\text{N}_4(90\%)$ and $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6(5\%)/g\text{-C}_3\text{N}_4(95\%)$, are very similar (figure 11): the high concentration of $g\text{-C}_3\text{N}_4$ influences the absorption band, narrowing it and shifting λ_{max} towards higher wavelengths. The long

absorption tails are still present, but are more intense for end-members composites, especially for g-C₃N₄(90%) heterojunctions.

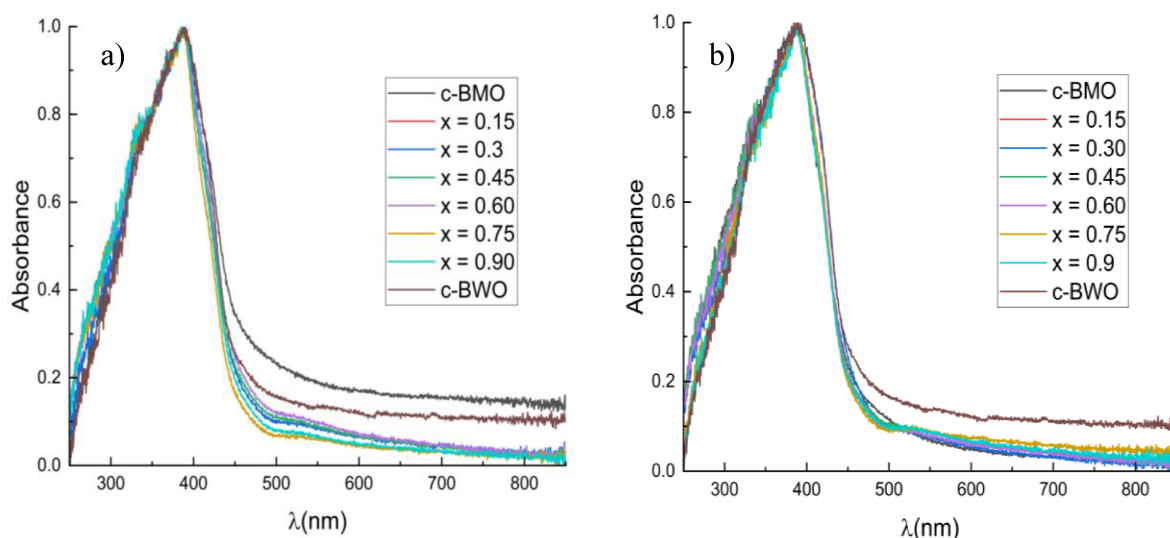


Figure 11. UV-Vis Absorption spectra of a) crystalline $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6(5\%)/\text{g-C}_3\text{N}_4(95\%)$ and b) crystalline $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6(10\%)/\text{g-C}_3\text{N}_4(90\%)$

Indirect band gaps (figure 12a) were calculated using Tauc plots: as expected, g-C₃N₄(95%) composites show a very linear trend and an average E_g of 2.72 eV, comparable with the ideal value of g-C₃N₄ (2.7 eV)^[28], while E_g of g-C₃N₄(90%) composites are much more dependent on the quantity of W contained in the solid solution. For $x \leq 0.3$, E_g is lower and similar to pure BMO, while $x \geq 0.45$ show higher band gaps, similar to pure BWO in values. The outlier nature of $\text{Bi}_2\text{Mo}_{0.25}\text{W}_{0.75}\text{O}_6$ is still recognizable even in low quantities.

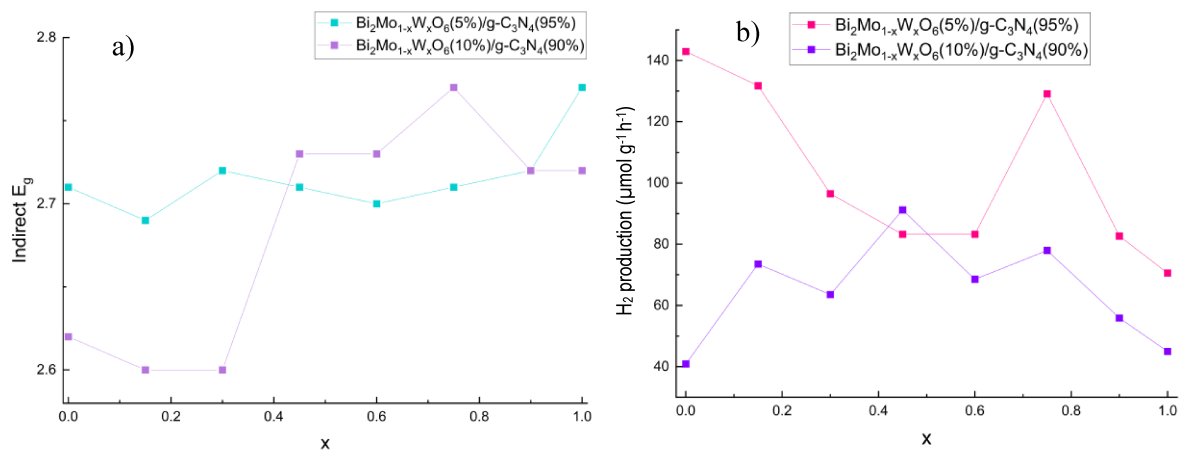


Figure 12 – A) Indirect band gaps and **B)** hydrogen productions of crystalline $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6(10\%)/\text{g-C}_3\text{N}_4(90\%)$ and $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6(5\%)/\text{g-C}_3\text{N}_4(95\%)$ series of heterojunctions in function of x (quantity of W)

Hydrogen production yields (figure 12b) are notably different for the two heterojunction series. g-C₃N₄(90%) heterojunctions show a very interesting trend: all solid solutions produce more H₂ than the pure end-members, with $Bi_2Mo_{0.55}W_{0.45}O_6$ (10%)/g-C₃N₄(90%) being the best performer ($\sim 91.2 \mu mol/g/h$), more than double that of BMO(10%) and BWO(10%).

While the band gaps of the heterojunctions are very similar to pure g-C₃N₄, the hydrogen yields from samples in the $Bi_2Mo_{1-x}W_xO_6$ (5%)/g-C₃N₄(95%) tend to decrease linearly with the increase of x: the best performing sample remaining Bi_2MoO_6 , but $Bi_2Mo_{0.25}W_{0.75}O_6$ (5%)/g-C₃N₄(95%) shows a much higher H₂ production than expected.

If we analyse hydrogen production vs band-gap (figure S6), $Bi_2Mo_{1-x}W_xO_6$ (10%)/g-C₃N₄(90%) shows that the best performing heterojunctions presents band-gaps far away in value from 2.7 eV: 2.60 eV for x=0.15, 2.73 eV for x=0.45, and 2.77 eV for x=0.75. Three sets of samples share the same band-gaps (2.60 eV for x=0.15 and 0.30; 2.73 eV for x=0.45 and 0.60; 2.72 eV for x=0.9 and 1), but it's always the sample containing a lower quantity of W that performs better: the best performing Mo:W ratio (0.45/0.55) show the increased charge transfer efficiency caused by reduced planar spacing without the increased charge-carrier recombination due to lattice distortion.^[12]

3. Conclusions

In this work we studied the photocatalytic water-splitting and nitrogen photofixation performance under simulated solar light of heterojunctions composed by g-C₃N₄ and Aurivillius oxides: amorphous and crystalline Bi₂MoO₆, Bi₂WO₆ and their solid solution series $Bi_2Mo_{1-x}W_xO_6$ (with x = 0.15, 0.3, 0.45, 0.6, 0.75, 0.9).

We evinced from PNF trials that quantifiable amounts of NH₃ are produced when Bi₂MO₆ is coupled with another co-catalysts, in this case g-C₃N₄, and that the different variables we considered (crystallinity of the Aurivillius material, transition metal and ratio between Bi₂MO₆ and g-C₃N₄) interact with each other in complex ways: it's interesting to note, when crystallinity is the only

variable, that the amorphous and crystalline series of the same oxide both show mirrored NH_3 yields and E_g values. The best performing heterojunctions is a-BMO(2.5%)/g-C₃N₄(97.5%) with an ammonia yield of 9 $\mu\text{mol g}^{-1}\text{h}^{-1}$. Both crystalline and amorphous BMO produce more ammonia when they're in lower quantities, with the best performing ratio of c-BMO (5%) being the worst for a-BMO and viceversa (2.5%). C-BWO shows better results for wt% at the far ends of the series (20 and 2.5%, with 2.5% being the second best performing composite overall for PNF), while a-BWO's yield peaks when wt% is 5%.

PHE trials highlight that Bi_2MoO_6 oxides tend to be more selective towards NRR than HER: all heterojunctions show an increasing hydrogen yields with the decrease in quantity of Bi_2MoO_6 . This trend is mostly linear, other than c-BMO(10%)/g-C₃N₄(90%), whose narrow band gap sharply lower the hydrogen yields under the worst performing heterojunction. The best performing sample is a-BMO(2.5%)/g-C₃N₄(97.5%), with a hydrogen yield of 145.4 $\mu\text{mol g}^{-1}\text{h}^{-1}$ (slightly higher than pure g-C₃N₄ nanosheets); the same composite turns out to be the best performer overall.

Further investigation of the photocatalytic water-splitting performance of $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$ (10%)/g-C₃N₄(90%) and $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$ (5%)/g-C₃N₄(95%) show that introducing lattice distortion can actually enhance photocatalytic activity. $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$ (10%)/g-C₃N₄(90%) hydrogen productions increases and decreases, creating a peak and valley trend: all solid solutions produce more hydrogen in comparison with end-members, with $\text{Bi}_2\text{Mo}_{0.55}\text{W}_{0.45}\text{O}_6$ (10%)/g-C₃N₄(90%) as the best performing. $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$ (5%)/g-C₃N₄(95%)'s H_2 production decreases with the increase of x (W wt%) pretty linearly, but when $x=0.75$, hydrogen production increases sharply and reaches 130 $\mu\text{mol g}^{-1}\text{h}^{-1}$ (nearly reaching Bi_2MoO_6 (5%) yield and nearly doubling Bi_2WO_6 (5%) yield).

This work furthers investigations on the complexity of interactions between the different physiochemical features of a material and how they affect the photocatalytic response of a simple binary heterojunction.

Supplementary informations

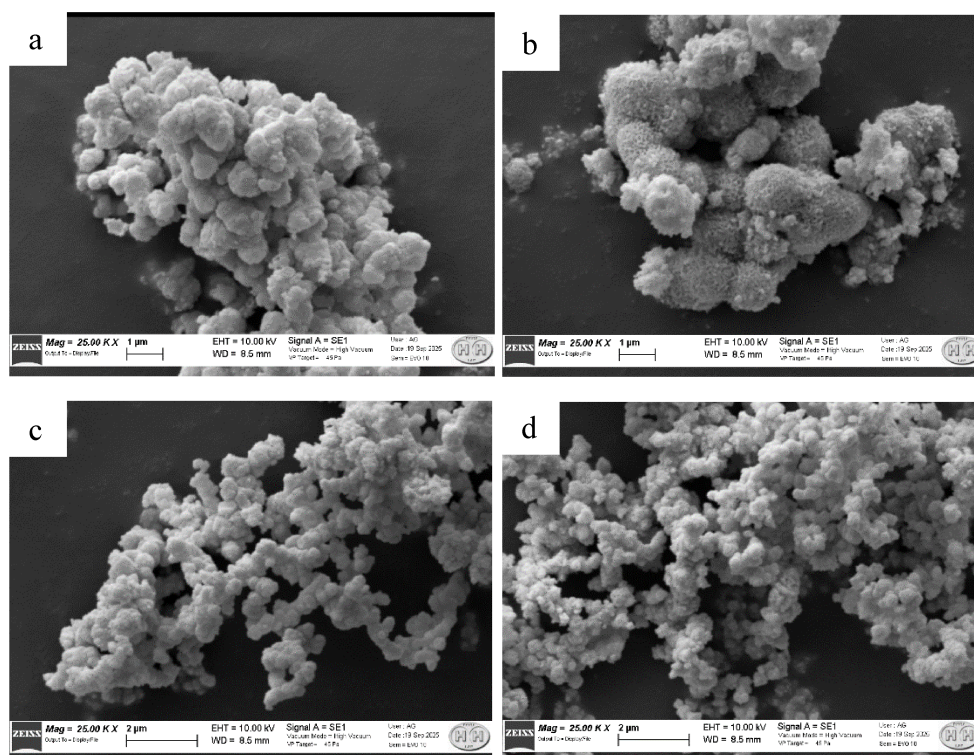


Figure S1. SEM pictures of a) amorphous and b) crystalline Bi_2MoO_6 , and c) amorphous and d) crystalline Bi_2WO_6

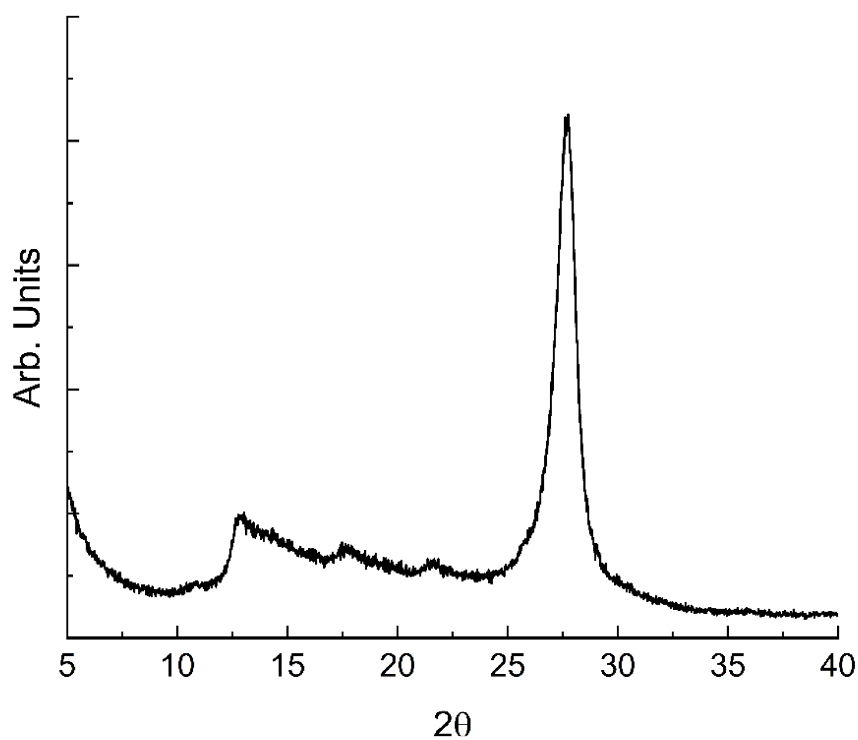


Figure S2. X-Ray Diffraction pattern of pure $\text{g-C}_3\text{N}_4$

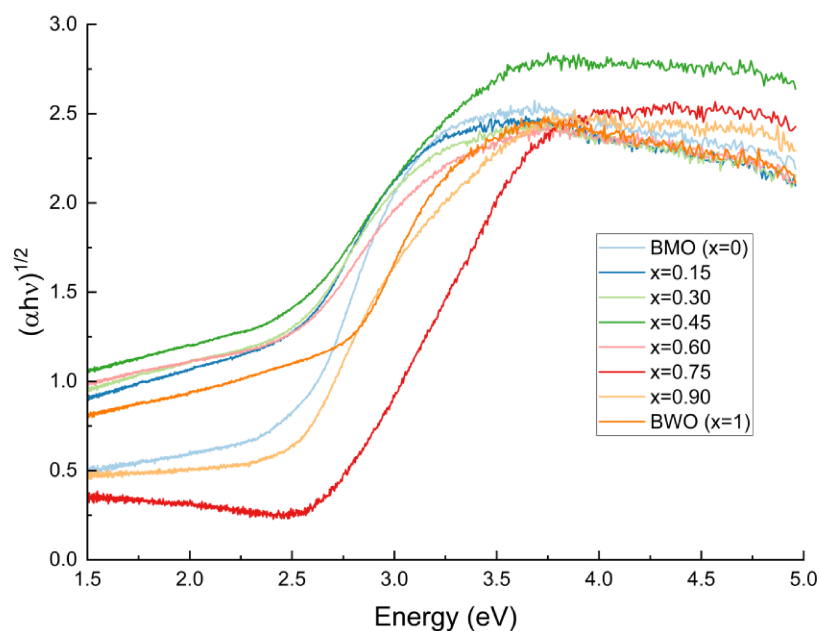


Figure S3. Tauc plots of the solid solution series $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$

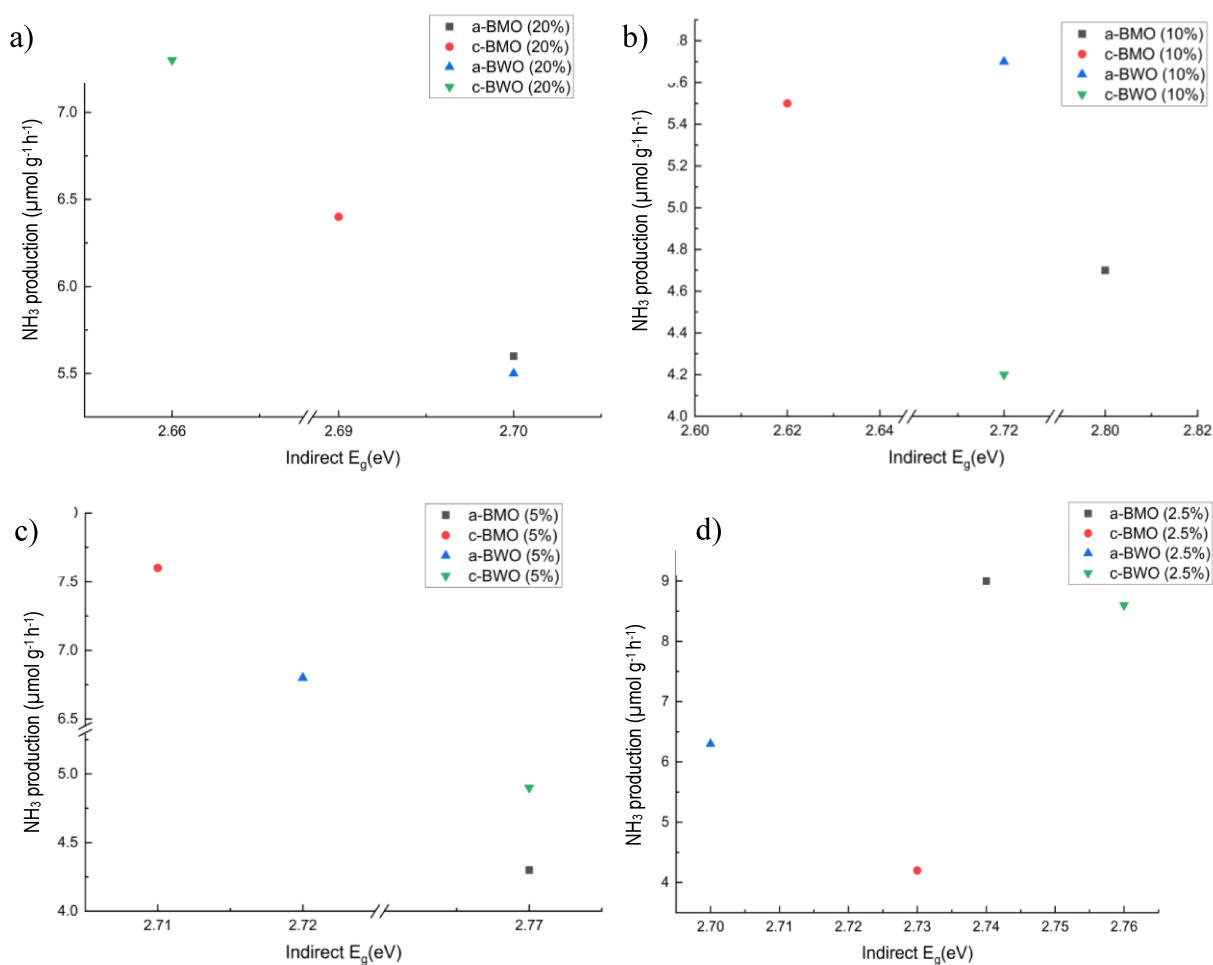


Figure S4. NH_3 production vs Indirect band gaps for a) $\text{g-C}_3\text{N}_4$ (80%) heterojunctions, b) $\text{g-C}_3\text{N}_4$ (90%) heterojunctions, c) $\text{g-C}_3\text{N}_4$ (95%) heterojunctions and d) $\text{g-C}_3\text{N}_4$ (97.5%) heterojunctions

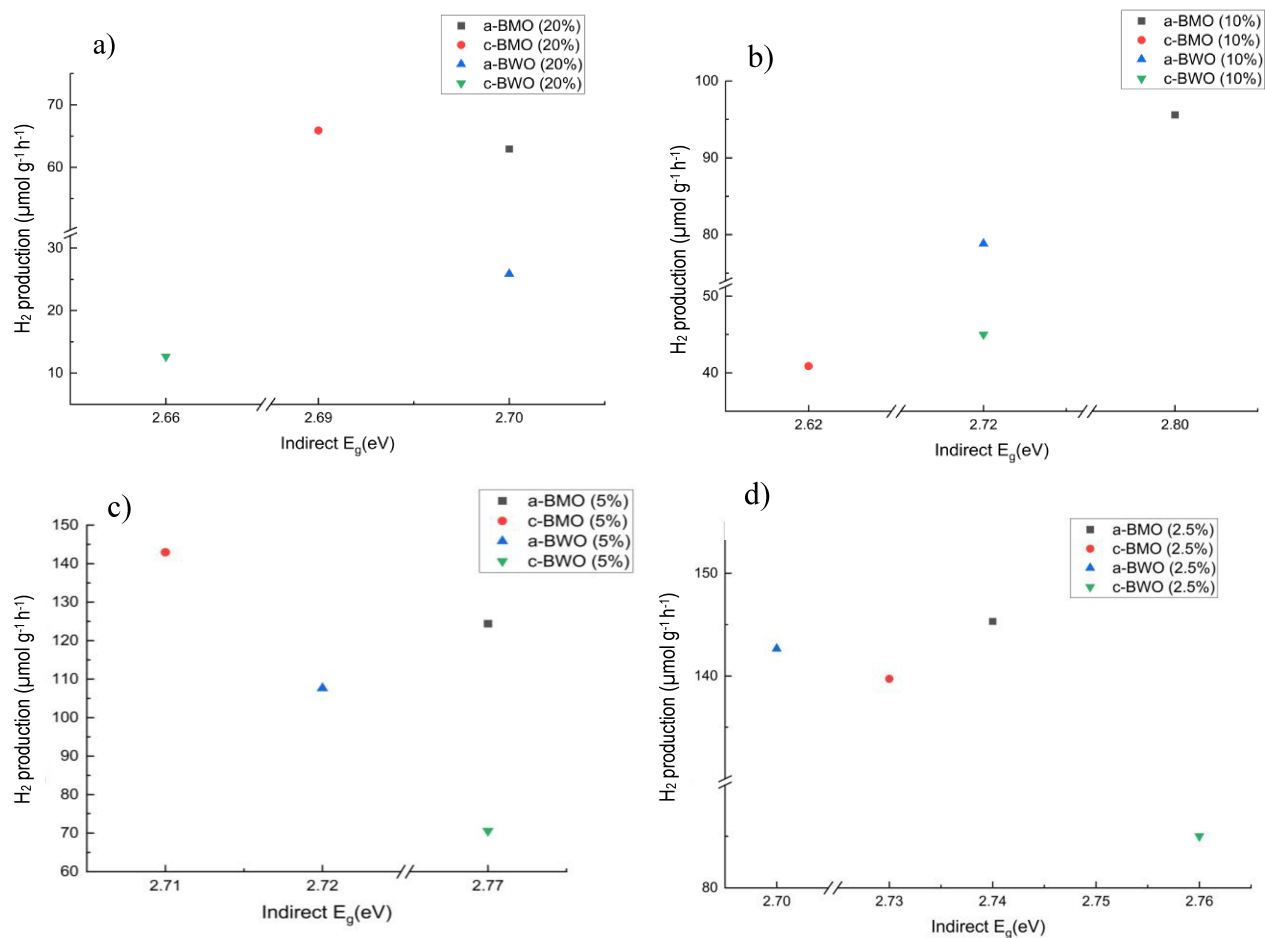


Figure S5. H₂ production vs Indirect band gaps for a) g-C₃N₄ (80%) heterojunctions, b) g-C₃N₄ (90%) heterojunctions, c) g-C₃N₄ (95%) heterojunctions and d) g-C₃N₄ (97.5%) heterojunctions

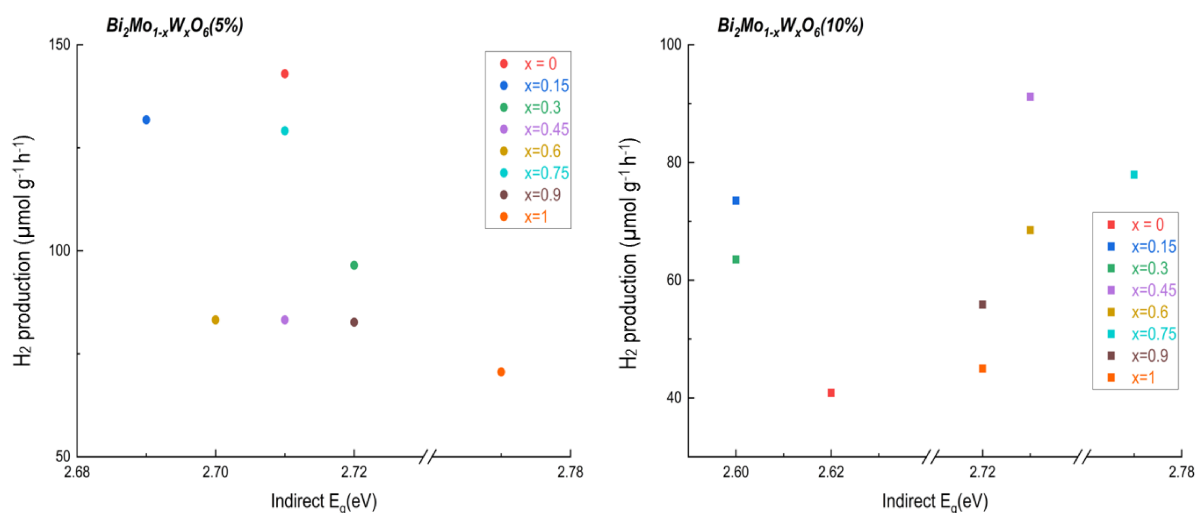


Figure S6. H₂ production vs Indirect band gaps for a) Bi₂Mo_{1-x}W_xO₆ (5%)/g-C₃N₄ (95%) heterojunctions and b) Bi₂Mo_{1-x}W_xO₆ (10%)/g-C₃N₄ (90%) heterojunctions

Table S1. Cell parameters obtained through Rietveld refinement of solid solutions $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$

x (wt% of W)	a(Å)	b(Å)	c(Å)	Cell volume(Å ³)
0	5.4974(5)	16.213(1)	5.5176(7)	491.77(8)
0.15	5.4879(5)	16.259(1)	5.5060(5)	491.27(6)
0.3	5.4755(6)	16.286(1)	5.4946(4)	489.98(7)
0.45	5.4487(6)	16.482(2)	5.4835(7)	489.98(7)
0.6	5.4510(5)	16.442(1)	5.4658(3)	489.85(7)
0.75	5.4540(6)	16.450(1)	5.4679(4)	490.56(8)
0.9	5.4512(6)	16.446(1)	5.4655(4)	489.97(6)
1	5.4446(3)	16.4454(7)	5.4650(3)	489.33(5)

Table S2. NH_3 production of amorphous and crystalline $\text{Bi}_2\text{MoO}_6/\text{g-C}_3\text{N}_4$ heterojunctions

	NH_3 production ($\mu\text{mol g}^{-1} \text{h}^{-1}$)			
Bi_2MoO_6 (wt%)	a-Bi₂MoO₆	c-Bi₂MoO₆	a-Bi₂WO₆	c-Bi₂WO₆
20	5.6	6.4	5.5	7.3
10	4.7	5.5	5.7	4.2
5	4.3	7.6	6.8	4.9
2.5	9	4.2	6.3	8.6

Table S3. H_2 production of amorphous and crystalline $\text{Bi}_2\text{MoO}_6/\text{g-C}_3\text{N}_4$ heterojunctions

	H_2 production ($\mu\text{mol g}^{-1} \text{h}^{-1}$)			
Bi_2MoO_6 (wt%)	a-Bi₂MoO₆	c-Bi₂MoO₆	a-Bi₂WO₆	c-Bi₂WO₆
100	0	0	7.9	0
20	63	65.9	25.9	12.6
10	95.6	40.9	78.8	45
5	124.5	143	107.7	70.6
2.5	145.4	139.7	142.7	85
0	143.2	143.2	143.2	143.2

Table S4. H₂ production of Bi₂Mo_{1-x}W_xO₆(10%)/g-C₃N₄(90%) and Bi₂Mo_{1-x}W_xO₆(5%)/g-C₃N₄(95%) heterojunctions

	H ₂ production (μmol g ⁻¹ h ⁻¹)	
x	Bi ₂ Mo _{1-x} W _x O ₆ (10%)	Bi ₂ Mo _{1-x} W _x O ₆ (5%)
0	40.9	143.0
0.15	73.5	131.8
0.3	63.5	96.5
0.45	91.2	83.2
0.6	68.5	83.2
0.75	78.0	129.1

Experimental Section

Sample synthesis and characterization

Amorphous and crystalline Bi₂Mo_{1-x}W_xO₆

Amorphous Bi₂MoO₆, Bi₂WO₆ and their solid solutions Bi₂Mo_{1-x}W_xO₆ have been synthesized using a simple solvothermal method: solution A is made by stirring, at ambient T, 2 mmol of Bi(NO₃)₃ · 5H₂O in 20 ml of ethylene glycol until it's clear; solution B is made in the same way but using 1 mmol of Na₂WO₄, Na₂MoO₄ or a mix of the two reagents in the stoichiometric quantity needed for the desired solution. Solution B is added to solution A and the obtained clear solution is left stirring for 30 minutes and then poured into a Teflon-lined stainless-steel autoclave and then left at 120°C for 24 hours. The obtained solid is filtered, washed and then dried overnight. The amorphous solid obtained is then subjected to a thermal treatment: 450°C for 3 hours in a muffle furnace. The solid solutions series has been made by changing the percentage of W in Bi₂Mo_{1-x}W_xO₆ with $x = 0.15, 0.30, 0.45, 0.60, 0.75$ and 0.90.

gC₃N₄ bulk and nanosheets

g-C₃N₄ nanosheets have been synthesized starting from the bulk form (bulk g-C₃N₄).

Dicyandiamine DCD (NH₂C(=NH)NHCN, Aldrich, 99%) is polymerized under N₂ flux: the alumina boat containing densely packed DCD is positioned in a quartz tube, filled with nitrogen, and heated up in a tubular oven (4 °C min⁻¹) to the selected temperature of 550 °C, followed by an isothermal step 4 hours long and finally cooled to room temperature (6 °C min⁻¹).

To produce thermally exfoliated nanosheets, 1 gm of finely ground bulk g-C₃N₄ was placed in an alumina boat (20 mL), spread to cover homogenously the bottom, and heated (5 °C min⁻¹) in a tubular oven under air until the desired temperature was reached. The boat was left at the desired temperature for 2 h and then cooled (6 °C min⁻¹) until reaching room temperature.

Bi₂Mo_{1-x}W_xO₆/nanosheets g-C₃N₄ composites

The *Bi₂Mo_{1-x}W_xO₆/nanosheets g-C₃N₄* composites have been synthesized by sonicating both powders in ethanol for 2 hours until they're finely dispersed, then the *Bi₂Mo_{1-x}W_xO₆* dispersion is added drop-by-drop into the stirring g-C₃N₄ dispersion. The mixture is stirred overnight at ambient temperature. The mixture is then centrifuged, washed, filtered and dried overnight. The different series have been realized by changing the percentage of the *Bi₂Mo_{1-x}W_xO₆* in the composites *Bi₂Mo_{1-x}W_xO₆/nanosheets g-C₃N₄*: 20, 10, 5, 2.5.

The crystal structure of the samples has been characterized by a Bruker D2 θ - θ diffractometer equipped with a Cu X-ray tube (Cu K α , λ = 1.5418 Å) and a linear position sensitive detector, depositing ~50 mg of the powders in a Si zero-background sample-holder and acquiring the measurements in the 10-70° 2 θ range, with steps of 0.01° and a time per step of 2 s.

Literature information were used for assigning space group and unit cell parameters of the characterized compounds. Nonetheless, their correctness was verified first by a visual powder pattern comparison, then by performing whole powder pattern refinements with the Le Bail approach on the XRD data acquired in our lab. UV-Vis Absorption spectra were acquired in the wavelength range 300-800 nm directly on the powders by using a Jasco V-750 spectrophotometer, equipped with an integrating sphere (Jasco ISV-922). Microstructural characterization of the samples was made using a high-resolution scanning electron microscope (SEM, TESCAN Mira 3) operated at 25 kV.

Nitrogen Photofixation Experiments and Ammonia Determination

N₂ photofixation experiments were conducted in tridistilled water containing 10% (v/v) methanol (Aldrich, $\geq 99.9\%$) irradiated in a Pyrex glass container (250 mL capacity, 100 mL sample). Methanol plays the role of sacrificial agent, whose job is to minimize the recombination of electron and holes – by being oxidized faster than water – and maximize electron extraction. After addition of the catalyst (0.5 g L⁻¹), the sample suspension was deoxygenated by N₂ bubbling (45 min) to obtain a saturated solution and then irradiated under magnetic stirring for 3 hours maintaining the temperature at 15°C. Irradiation was performed under simulated solar light (1500 W Xenon lamp, 300-800 nm) using a Solar Box 1500e (CO.FO.ME.GRA S.r.l.) at 500 W/m².

The quantification was performed with ammonia ion selective electrode (ISE), which guarantees accurate detection over colorimetric methods (e.g. Nessler method) as previously assessed.^[1,2] The Thermo Scientific Orion Ammonia Ion Selective Electrode (ISE) was selected as it measures ammonia ions in aqueous solutions quickly, simply, economically, and accurately. It uses a hydrophobic gas-permeable membrane which separates the sample solution from the electrode filling solution. Water does not wet the membrane and does not penetrate the holes, whereas the dissolved ammonia in the sample solution diffuses through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. In any sample the partial pressure of ammonia is proportional to its concentration.

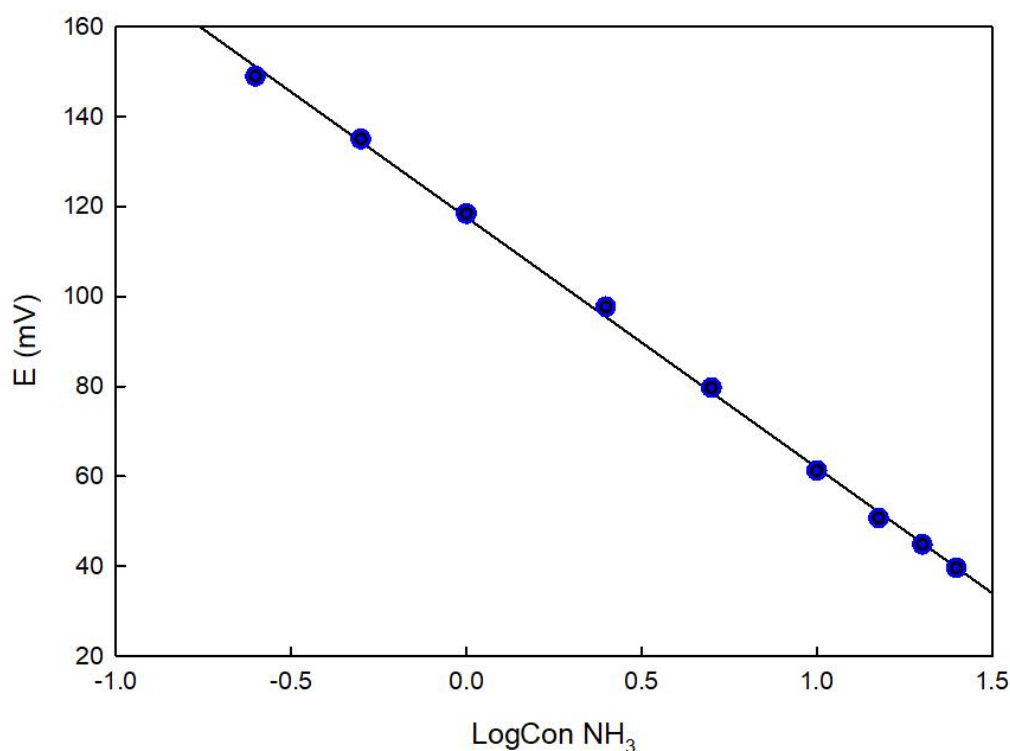


Figure S7. Mean calibration curve (n=7) for ammonia quantification ($0.25 \text{ mg L}^{-1} \div 25 \text{ mg L}^{-1}$ as NH_3).

All measurements were performed in a beaker with minimized surface area/volume ratio, at a uniform and moderate rate, under controlled temperature. Since temperature changes can cause a change of the slope and potential, a piece of insulating material, e.g., ceramic or cardboard, was placed between the magnetic stirring plate and beaker to prevent measurement errors because of a heat transfer to the sample. In details, ISE was immersed in the solution (standard or sample, 1% v/v 10 N NaOH, 10% v/v MeOH) until a stable potential value (mV) was obtained. For the quantification, a calibration curve was constructed daily plotting the mV value recorded after 2 minutes equilibration time against the Log Concentration, to verify the slope (varying in the range $-54 \div -60 \text{ mV}$). The ammonia

concentration in the sample was further assessed by two standard additions. Figure S7 reports an example of mean calibration curve ($0.25 \text{ mg L}^{-1} \div 10 \text{ mg L}^{-1}$ as NH_3).

Photocatalytic Water-Splitting experiments and Hydrogen determination

Hydrogen evolution experiments took place in Pyrex glass containers (25 mL) containing 20 mL of an aqueous solution 10 % (v/v) triethanolamine (TEOA, Aldrich, $\geq 99\%$), where TEOA plays the role of sacrificial agent, and 20 mg of the photocatalyst (1 g catalyst/L solution). Oxygen was removed by Nitrogen bubbling for 20 minutes, during which the reactor stand in a ultrasound bath. All experiments were carried on in the presence of 1% of Pt, 41 μL of a 0.025 M H_2PtCl_6 solution (hexachloroplatinic acid hydrate, 38 % Pt basis, Sigma Aldrich) as the Pt co-catalyst precursor (in situ photodeposited on the catalyst during irradiation) was added to the suspension after 18 minutes of bubbling and sonicating and then left degassing for 2 additional minutes. The photoreactors were sealed using sleeve stopper septa. Irradiation was performed under simulated solar light (1500 W Xenon lamp, 00-800 nm) using a Solar Box 1500e (CO.FO.ME.GRA S.r.l.) at 500 W/m^2 for 4 hours. The headspace evolved gas was quantified by gas chromatography (using a molecular sieve column characterized by a length of 30 m, an internal diameter of 0.53 mm, and a film thickness of 50 μm), coupled to thermal conductivity detection (GC-TCD). 250 μL of gas drawn up from the reactor headspace in injected in the Gas Chromatographer. The H_2 evolution is expressed as $\mu\text{mol g}^{-1} \text{ h}^{-1}$.

The first-author Giulia Giovilli, author of the present Ph.D. work, carried out the synthesis and characterization of the solid solutions and their heterojunction, and the quantification of photocatalytic H₂ produced.

The present work is in preparation for publication

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Chapter 5

Conclusions and outlooks

Considering the results obtained in previous chapters, this work highlights the versatility of g-C₃N₄ – the pre-eminent eco-friendly and non-critical raw material-based VLD photocatalyst – in the construction of heterojunction systems for the photocatalytic production of green ammonia and hydrogen, as developing innovative materials to satisfy global energetic needs become more and more essential for the future. The work of this Ph.D. thesis investigates three distinct heterostructured systems containing g-C₃N₄ – exemplifying how different modification methods affect the photocatalytic activity of the material – and the complex way the traits of heterojunction's components interact with each other in the final product.

Experimental results reveal that heterojunction engineering and morphological tuning promote efficient charge separation and transfer, and also suppress charge recombination—one of the key limitations of graphitic carbon nitride, and of most photocatalysts, that is currently under extensive investigation.

Chapter 2, “Mechanistic Insight into the Nitrogen Photofixation Reaction by BiOBr-based Heterojunctions” was dedicated to the investigation of the photocatalytic nitrogen fixation activity of the BiOBr/g-C₃N₄ heterojunctions under simulated solar light. The entire compositional range with wt% of BiOBr 100, 90, 75, 60, 45, 30, 15, 10, and 0 was synthesized by co-precipitation of bismuth nitrate and potassium bromine in a water-acetic acid solution containing dispersed g-CN nanosheets (exfoliated at 500°C from bulk g-CN). The obtained heterojunctions show a marked improvement in the ammonia production rates, with BiOBr(10%)/ g-C₃N₄ (90%) exhibiting a production of ~20 μmol g⁻¹ h⁻¹ - nearly seven times higher than pristine g-C₃N₄ and more than twice that of pure BiOBr - while maintaining excellent structural and morphological stability over multiple reaction cycles. Photoluminescence quenching, extended carrier lifetimes observed in transient absorption

spectroscopy, and band alignment analysis confirmed that the enhanced photocatalytic activity is owed to the improved charge separation and transfer efficiency of the composite. Density functional theory (DFT) calculations provided deeper mechanistic insight, revealing that the superior performance could be linked to the exposure of the less stable but more catalytically active BiOBr (010) surface, while the more stable BiOBr (001) surface exhibits an energy barrier for nitrogen reduction, explaining the performance drop observed at higher BiOBr loadings where growth along the (001) direction dominates. The observed synergy between g-C₃N₄ and BiOBr, especially at low BiOBr loading, offers a sustainable path forward by reducing reliance on heavy bismuth content while achieving high activity. This work advances our understanding of nitrogen photofixation mechanisms and provides a foundation for the development of efficient, scalable, and environmentally benign routes for solar-driven ammonia production.

Chapter 3, “Synthesis and Characterization of g-C₃N₄/Metal NPs Based Composites for the Photocatalytic Production of Hydrogen” is centered on the systematic optimization of metallic NPs-decorated g-C₃N₄ used for photocatalytic water-splitting in absence of Pt co-catalyst. We started by investigating how different wt% of Ag nanoparticles (1, 0.4 and 0.1%) modify the hydrogen production rate of g-C₃N₄ nanosheets, obtained through liquid exfoliation, both with and without thiol functionalization. Because Ag(0.1%) is the best weight ratio for both functionalized and non-functionalized g-C₃N₄, liquid exfoliated nanosheets were substituted in the heterojunction with thermally exfoliated ones (with T of exfoliation = 500, 525 and 550°C) and decorated with 0.1% wt of Ag NPs, to draw a comparison between the two methods of exfoliation. The optimal performance is achieved with g-C₃N₄(525°C)/Ag_{0.1%}, with a hydrogen evolution rate of ~70 μmol g⁻¹ h⁻¹, nearly three times higher than SH-g-C₃N₄/Ag_{0.1%} and nearly five times higher than g-C₃N₄/Ag_{0.1%}. In addition, it shows that thermal exfoliation makes thiol functionalization moot: all SH-g-C₃N₄(T)/Ag_{0.1%} produce less hydrogen than SH-g-C₃N₄/Ag_{0.1%}. Thermal exfoliation not only reduce the thickness of g-C₃N₄ nanosheets, but also introduces pores and C and N vacancies on the surface of the material, increasing the number of active sites for hydrogen reduction, but also for NPs

decoration. Adding thiol groups on top of that means overloading the material and decreasing its light absorption, because the entire surface is covered; the same happens for g-C₃N₄ nanosheets exfoliated at 550°C. The opposite happens when Ag nanoparticles are exchanged for Au nanospheres and nanorods in g-C₃N₄/Au_{0.1%} : the hydrogen yield is lower (respectively two and three times less), because 0.1% wt of Au nanoparticles covers less surface area than 0.1% wt of Ag nanoparticles. This work highlights the importance of subsequent tuning of different physicochemical characteristics to build an optimized heterojunction for photocatalytic applications: a middle ground needs to be found when optimizing different characteristics of a heterojunction, because modifying just one thing will bring on waterfall changes. In addition, this research highlights that metallic NPs can be used as a substitute of Pt in PHE, but further research is needed to find a configuration that works as well.

Chapter 4, “g-C₃N₄/Bi₂MO₆ (M = Mo, W, Mo_{1-x}W_x) Heterojunctions for Solar-Driven Photocatalytic Nitrogen and Hydrogen Production” investigates g-C₃N₄ nanosheet-based heterojunctions built with Aurivillius oxides, containing variable amounts of W and Mo, and applied to both solar-driven PNF and PHE. Ammonia production trials actually show that heterojunctions are needed for the photocatalysis product to form in quantity high enough to be measured; in this first set of trials, three different variables are taken in consideration: crystallinity of Bi₂MO₆, transition metal M (W o Mo), and the wt% of Bi₂MO₆. They interact in complex ways, but it’s notable that, when either the crystallinity or the transition metal M is fixed, the NH₃ production vs g-C₃N₄ wt% trend is mirrored: for the highest Bi₂MO₆ wt%, the photocatalytic activity depends mostly on the transition metal, but only for crystalline oxides (amorphous materials have the same band gap and same ammonia production rate); for Bi₂MO₆ wt% under 20%, the photocatalytic activity depends on the interaction forged between the two variables.

Hydrogen production is tightly bound to the amount of g-C₃N₄ contained in the composite: the higher it is, the higher is the quantity of H₂ produced. c-BWO/g-C₃N₄ is consistently the worst performing composite at every wt%, while a-BWO, a-BMO and c-BMO show a linear increase with

very similar hydrogen production at the lowest wt%. The only outlier is c-BMO(10%)/g-C₃N₄(90%), whose production is actually even lower than c-BMO(10%)/g-C₃N₄(90%): combined with the reduction of the overpotential of CB and VB, the band gap is narrow enough to promote the recombination of charge carriers, thus lowering the photocatalytic activity of the material.

The best performing sample for both PHE and PNF is a-BMO (2.5%) – g-C₃N₄ (97.5%), with a hydrogen yield of 145.4 $\mu\text{mol g}^{-1}\text{h}^{-1}$ (slightly more than pure g-C₃N₄ nanosheets) and ammonia yield of 9 $\mu\text{mol g}^{-1}\text{h}^{-1}$ (three times the one of pure g-C₃N₄ nanosheets).

Further investigation of the photocatalytic water-splitting performance of $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$ (10%)/g-C₃N₄(90%) and $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$ (5%)/g-C₃N₄(95%) show that introducing lattice distortion enhances photocatalytic activity. $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$ (10%)/g-C₃N₄(90%) hydrogen productions increases and decreases, creating a peak and valley trend: all solid solutions produce more hydrogen in comparison to end-members, with $\text{Bi}_2\text{Mo}_{0.55}\text{W}_{0.45}\text{O}_6$ (10%)/g-C₃N₄(90%) as the best performing. $\text{Bi}_2\text{Mo}_{1-x}\text{W}_x\text{O}_6$ (5%)/g-C₃N₄(95%)’s H₂ production decreases with the increase of x (W wt%) pretty linearly, but when x=0.75, hydrogen production increases sharply and reaches 130 $\mu\text{mol/g/h}$ (nearly reaching Bi₂MoO₆ (5%)’s results and nearly doubling Bi₂WO₆ (5%)’s).

This work furthers investigations on the complexity of interactions between different physiochemical characteristic of one component of the heterostructure and highlights how they affect the photocatalytic response of a simple binary heterojunction. It also shows that introducing a lattice distortion can have impressive results on the photocatalytic activity of a semiconductor.

These results cement g-C₃N₄ as a versatile and highly tunable material, even when, on the surface, it’s coupled in simple binary heterojunctions. A systematic investigation of how different materials interact with each other based on varying physiochemical features is necessary to determine the best configuration for enhancing the photocatalytic activity of a composite. Increasing light harvesting, improving surface reaction kinetics, and optimizing band alignment are all improvements that can be made through a variety of methods and, as we have seen in previous chapters, combining different

modifying strategies is necessary to fully optimize a heterojunction for a specific photocatalytic application. In conclusion, research emphasizes that tailoring different features of a simple heterojunction can be one of the most effective ways to improve its photocatalytic performance. Broadening the scope of this research field by pursuing emerging materials and innovative synthetic methods is needed to give solar-driven photocatalysis a fighting chance to become a commercially-applicable technology for the production of solar fuels.



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