

Review

The Challenges of Integrating the Principles of Green Chemistry and Green Engineering to Heterogeneous Photocatalysis to Treat Water and Produce Green H₂

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Abstract: Nowadays, heterogeneous photocatalysis for water treatment and hydrogen production are topics gaining interest for scientists and developers from different areas, such as environmental technology and material science. Most of the efforts and resources are devoted to the development of new photocatalyst materials, while the modeling and development of reaction systems allowing for upscaling the process to pilot or industrial scale are scarce. In this work, we present what is known on the upscaling of heterogeneous photocatalysis to purify water and to produce green H₂. The types of reactors successfully used in water treatment plants are presented as study cases. The challenges of upscaling the photocatalysis process to produce green H₂ are explored from the perspectives of (a) the adaptation of photoreactors, (b) the competitiveness of the process, and (c) safety. Throughout the text, Green Chemistry and Engineering Principles are described and discussed on how they are currently being applied to the heterogeneous photocatalysis process along with the challenges that are ahead. Lastly, the role of automation and high-throughput methods in the upscaling following the Green Principles is discussed.

Keywords: automation; green chemistry principles; green engineering principles; heterogeneous photocatalysis; hydrogen production; upscaling; water treatment



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1. Introduction

There are two milestones in heterogeneous photocatalysis [1]. First, the group of Muller successfully degraded isopropanol using ZnO under UV irradiation in 1969. Later, in 1972, the group of Fujishima and Honda were able to produce hydrogen via the water splitting reaction by irradiating TiO₂ with UV light. From 1975 to 1985, the first generation of photocatalysts (most of them TiO₂-based) was developed for H₂ production via the water splitting reaction, aiming at studying the semiconductor/solution interface under UV irradiation and looking for new and more efficient semiconductors. During the second-generation of photocatalysts (1986–2000), the investigation on modified semiconductors for a better response under visible light irradiation began [2], which was continued in the third generation that started in 2001 [3]. The corpus of literature was focused on modifying the photocatalysts by doping or coupling with other semiconductors to form heterostructures, including the S- and Z-schemes [4,5]. In environmental engineering, heterogeneous photocatalysis has been identified as a promising alternative for water purification and H₂ production [6–8]. Upon the irradiation of the semiconductor with light of proper energy, the electrons at the highest occupied molecular orbital (HOMO, the valence band) are excited and thus promoted to the lowest unoccupied molecular orbital (LUMO, the conduction band), resulting in the generation of the charge carriers known as the hole/electron pair (Equation (1)). Then, the charge carriers migrate to the surface of the crystalline semiconductor (Figure 1). Once there, the photo-holes (h⁺) react with the

adsorbed molecules, producing oxidative species. As shown in Equations (2) and (3), water molecules are oxidized to produce $\bullet\text{OH}$ species that react with organic pollutants resulting in intermediates and, at the best conditions, reaching the mineralization. In some cases, photo-holes can directly react with the adsorbed organic molecules (Equation (4)), although it depends on the nucleophilic nature of the reagents (e.g., the occurrence of aromatic rings or resonance structures within the molecule). The reactive oxygen species are able not only to degrade recalcitrant organic pollutants but also kill pathogens, oxidize heavy metals, and destroy antibiotic resistance genes (Figure 1) [9].

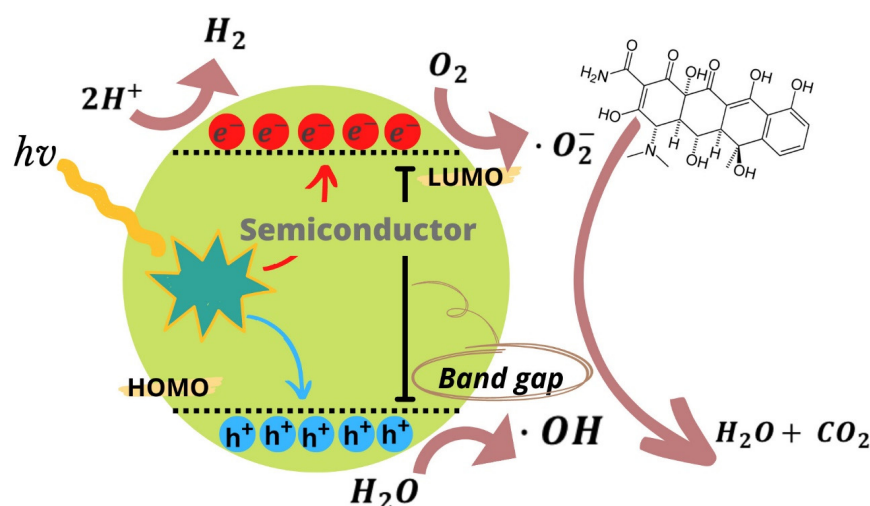
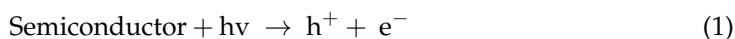
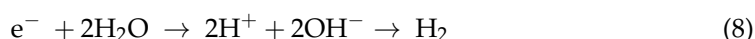
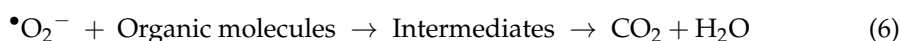


Figure 1. Heterogeneous photocatalytic process to degrade organic pollutants in water and green H_2 production through the water splitting reaction.

The photo-electrons in the conduction band react with the dissolved oxygen adsorbed on the surface of the photocatalyst, producing the superoxide species ($\bullet\text{O}_2^-$), which are capable to oxidize organic pollutants (Equations (5)–(6)). Additionally, photoelectrons can directly react with pollutants to generate intermediates (Equation (7)); this process will depend on the electrophilic nature of the organic molecules (e.g., sulfonic moieties). Under reductive conditions, the photoelectrons are able to produce H_2 through the water splitting reaction (Equation (8) and Figure 1).



To achieve this, the potential of the conduction band must be higher than that necessary for the H^+ reduction (i.e., 0 eV vs. NHE at pH = 0), plus an overpotential [10]. This condition constrains the number of semiconductors that can be used for H_2 production, with nitrides, halides, and calcogenides (e.g., metal sulfides) as the most commonly chosen materials [3,11]. In the photocatalytic water splitting reaction, the photo-holes in the valence band must be scavenged by nucleophilic molecules, known as sacrificial agents, in order

to avoid the re-oxidation of the produced hydrogen. The most commonly used sacrificial agents are light alcohols and carboxylic acids, sulfates, and other inorganic ions [10].

Overall, the photocatalytic process comprises three fundamental steps: (a) the absorption of light by the semiconductor producing the charge carriers; (b) the migration of the charge carriers to the surface of the crystal; and (c) the reaction of the reactive oxygen species and/or charge carriers with the adsorbed species to degrade organic pollutants and produce hydrogen (Figure 1). These steps are significantly affected by intrinsic material conditions, such as crystallinity, particle size, surface area, superficial charge, and optoelectronic properties, as well as the characteristics of the reaction medium, including pH, light penetration, composition, etc. Detailed information on these topics can be found in previous extensive reviews [12,13].

For benchmarking purposes, the International Organization for Standardization (ISO) has established five types of tests to assess the photocatalytic activity of ceramic materials, which are briefly described in Table 1.

Table 1. Recommended tests for photocatalytic materials according to the International Organization for Standardization.

Photocatalytic Test	ISO Reference
Anti-bacterial activity	ISO 27447:2019
Air purification	
Removal of NO	ISO 22197-1:2016
Removal of acetaldehyde	ISO 22197-2:2019
Removal of toluene	ISO 22197-3:2019
Self-cleaning performance	ISO 27448:2009
Water purification	
Generation of active oxygen species	ISO 10676:2010
Degradation of methylene blue	ISO 10678:2010
Dissolved oxygen consumption in a phenol solution	ISO 19722:2017

Through these tests, it is possible to compare the activity of photocatalysts under standardized conditions. However, some parts are severely outdated, since using the degradation of azo dyes is not completely appropriate to measure the photocatalytic efficiency, as this type of organic molecules can sensitize the semiconductor, resulting in an experimental artifact. To date, the list of standard tests does not include photocatalytic H₂ generation, although some documents (ISO 22734) suggest that some related tests are nearly ready.

Hydrogen is considered as a clean energy source due to its superior energy conversion compared to natural gas, while its combustion produces zero emissions of greenhouse gases [14]. Most of the commercially available H₂ is produced from different feedstocks, such as electricity, biomass, and fossil fuels [15,16]. It has made room for the development of cleaner processes to produce green H₂, with lower emissions and reduced energy inputs by harnessing the renewable sources and thus generating multiple desired outputs [14]. In this sense, producing green H₂ through the photocatalytic water splitting reaction is a cleaner process compared to other sources [17]. Moreover, wastewater can be valorized as a raw material for hydrogen production. This can be achieved either through the aqueous reforming process that converts light hydrocarbons and water into CO and H₂ at low temperatures [18,19] or by the heterogeneous photocatalysis process. For the latter, the dissolved organic matter, especially the light compounds, are used as sacrificial agents that impede the recombination of the photo-produced charge carriers at the time photo-electrons reduce the water molecule [20]. Even when the efficiency of the H₂ production is low, the conjunctive action of the oxidation—reduction reactions to purify water while producing green H₂ results in significant valorization of wastewater that is worth further investigation.

Currently, H₂ is mainly produced from fossil fuels and the cost is from 2 to 4 times less than H₂ production through the water splitting process [15]. For example, the costs

of producing hydrogen from conventional fossil fuels varies between 1.34–2.27 USD kg^{−1}, while using biomass as raw material costs between 1.77 and 2.05 USD kg^{−1} [21]. Conversely, the levelized cost of photocatalytic H₂ production was estimated as 18.32 USD kg^{−1} in 2021 (making some important assumptions, such as the remarkably high performance of the photocatalysts) [22]. To date, the efficiency of the photocatalytic water splitting reaction is below 1% (measured as the sun to hydrogen conversion, STH). Remarkable investigations are advancing to surpass this threshold and achieve more than 5% of STH conversion and, under this scenario, the cost in the production of green H₂ would decrease to 1.6–3.5 USD kg^{−1} [23].

Current research has been focused on the synthesis of highly efficient photocatalysts to remove organic pollutants from water and to produce green H₂ using low energy or renewable light sources, such as sunlight. We consider it is time to migrate from laboratory tests to upscaled systems, which include reaction systems testing real water and wastewater and microplant, pilot-plant, or industrial-scaled systems. As shown in Figure 2, through the last decade, most of the research has been centered on the synthesis of new photocatalysts, while the development of new photoreactors and the upscaling of the heterogeneous photocatalysis process have been left out.

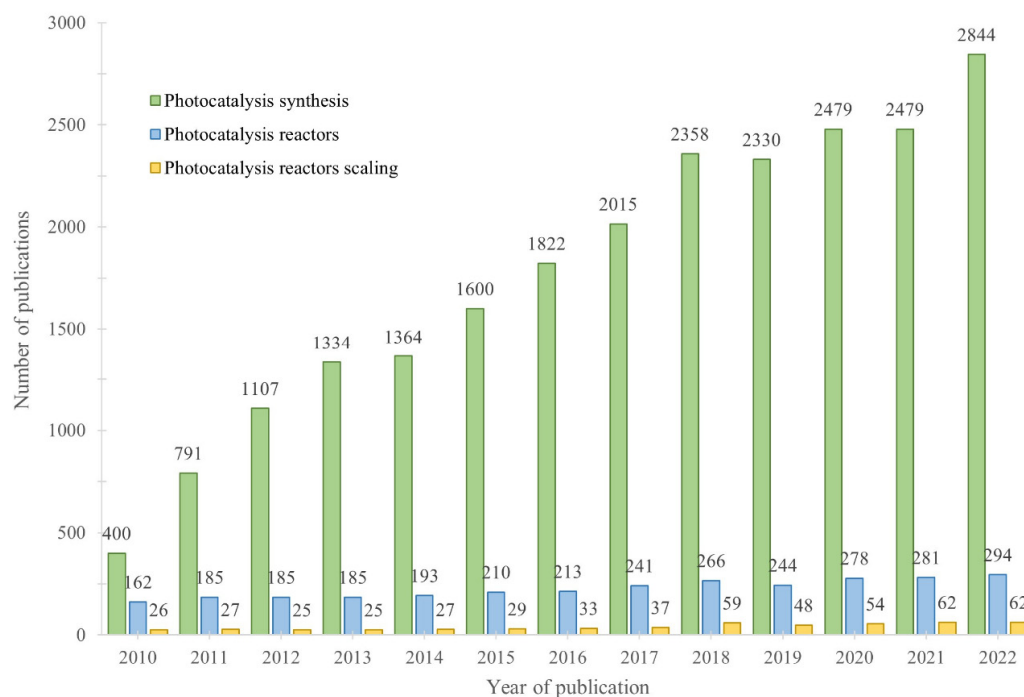


Figure 2. Comparison of the number of published studies on the synthesis of new photocatalysts (green bars), the development of photoreactors (blue bars), and the upscaling of the heterogeneous photocatalysis process (yellow bars). The search of the publication was performed in *Scopus* using the keywords “photocatalysis” + “synthesis”, “photocatalysis” + “reactors”, and “photocatalysis” + “reactors” + “scaling”.

Indeed, the discovery of new and highly effective photocatalysts through optimum synthetic routes and using high-throughput methods is a fertile field with new materials awaiting to be discovered. Nevertheless, the upscaling of photocatalytic reactors from the laboratory and pilot-scale is essential to globally implement these technologies, especially in regions with high sunlight irradiation. Mild and eco-friendly conditions must be prioritized to obtain sustainable upscaled systems, integrating Green Engineering and Green Chemistry Principles (GEP and GCP, respectively) to address environmental pollution and energy demand from a Life Cycle Analysis perspective [24], as these principles can be applied from the synthesis steps to the applications. Chemicals are unavoidable to achieve economic and social development, but their nature and mode of production can be tuned

in accordance to the Green Principles, paving the way for sustainable development and aiming at improving the productivity of the processes by minimizing their harm [25].

The main objective of this review is to explore the current state of the art on the upscaling of the heterogeneous photocatalysis process, as well as to identify the integration of the Green Principles for the discovery and synthesis of new photocatalysts and the upscaling itself. The currently identified and foreseen challenges in the upscaling of green heterogeneous photocatalysis process are described and briefly discussed.

2. Integrating the Green Principles to the Heterogeneous Photocatalytic Process

The concept of green chemistry was introduced by the United States Pollution Prevention Act (1990) and the Green Chemistry Principles (GCP) were presented by Paul Anastas and John Warner in their search for a safer synthesis method (Figure 3). On the other hand, the Green Engineering Principles (GEP) were developed in 2003 by Anastas and Zimmerman to complement the 12 GCPs with important concepts on environmental impact, providing with a life cycle perspective [25,26]. The current scenario of environmental pollution and the need for eco-friendly actions have promoted the infusion of the Green Principles in various scientific fields, intending to limit the excessive use of resources and hazardous chemicals and abolish any potentially harmful by-products or reduce their harmfulness. Considering the economic and environmental impacts, the Green Principles are employed in governmental monetary policies, industrial and technological management, and educational systems and practices [27–29]. For heterogeneous photocatalysis, the main objective of the GCPs is the production of eco-friendly photocatalysts that display a wide range of light absorption and high reaction performance, using soft synthetic processes.

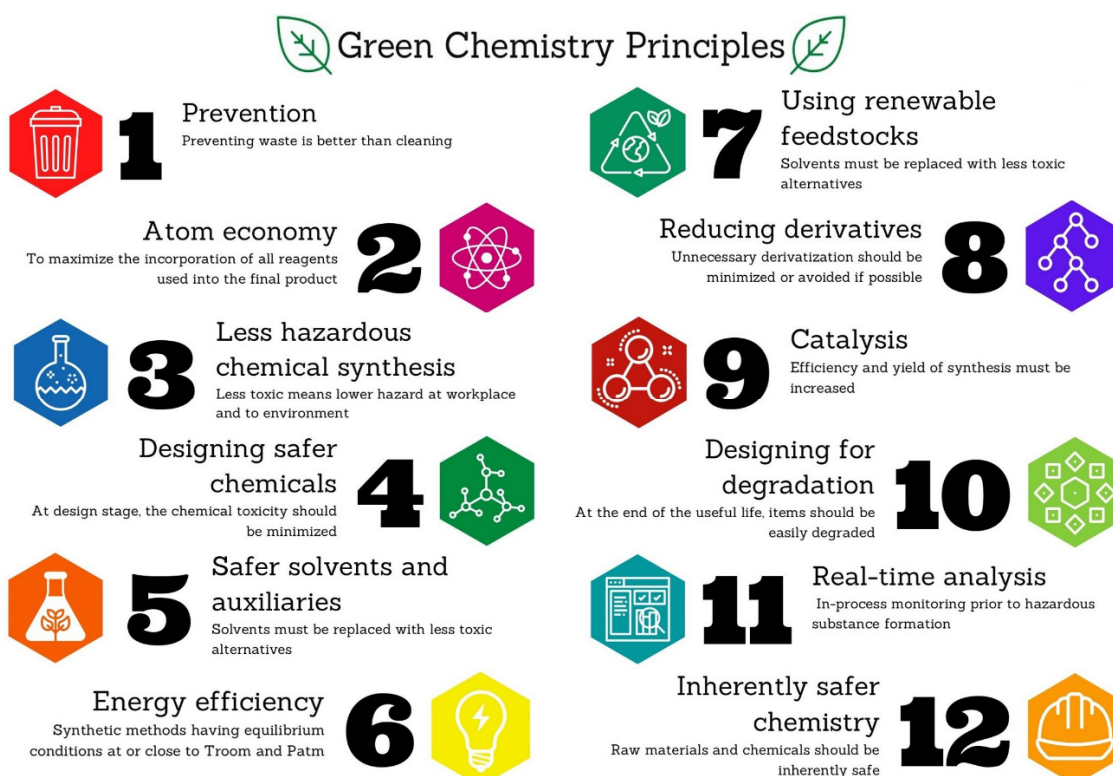


Figure 3. The Green Chemistry Principles (GCP, with information from [30]).

Heterogeneous photocatalysis to treat water and to produce green H_2 has the potential to be in line with some GCPs. For example, using minimal amounts of photocatalysts to achieve the complete mineralization of organic matter in water and to continuously produce green H_2 prevents waste rather than treating residues (GCP 1), which are actually produced in other process, such as adsorbents used in water treatment. Additionally, sev-

eral photocatalysts are produced using soft processes, generating less hazardous chemical syntheses (GCP 3). In fact, green chemistry is embedded in the synthesis of new photocatalysts [31] to achieve safer materials (GCP 4). The development of mild-conditions and soft synthesis process are comparatively less energy-consuming and sometimes they use renewable feedstocks, such as sunlight or microbial biomass [32–34] (GCPs 6 and 7). Lastly, some photocatalysts are designed to be safely disposed after they are exhausted (GCP 10); bismuth-based and iron-based materials are good examples of this [35–38]. When we think about an upscaled photoreactor, the synthesis of the adequate amount of catalyst must be considered [37]. The use of safer chemicals for the large-scale synthesis of photocatalysts with harmless by-products is the primary factor to be investigated. [39]. All the GCPs are interconnected and the basic idea is to adhere to environmentally friendly and energy-efficient approaches to prevent pollution and ensure a safer implementation of the process. This may constitute the commercialization of the photocatalytic processes without harming the environment. Additionally, the GCPs contribute to the circular economy that indicates the efficient use of resources from the production to recycling, with zero waste due to 100 percent utilization of the resources. Practicing the GCPs may stabilize the circular economy, balancing the environment with economic and society development [40]. By joining the GCPs with a circular economy, it is possible to achieve sustainable development goals [41].

Green Engineering Principles (Figure 4) provide a framework for scientists and engineers to design effective, ecologically intelligent materials, products, and systems in conjunction with GCPs. So far, the published works on the application of GEPs are very scarce compared to those focused on the synthesis and reaction processes adopting the GCPs. We consider that upscaling the heterogeneous photocatalysis process should be performed under both Green Principles.

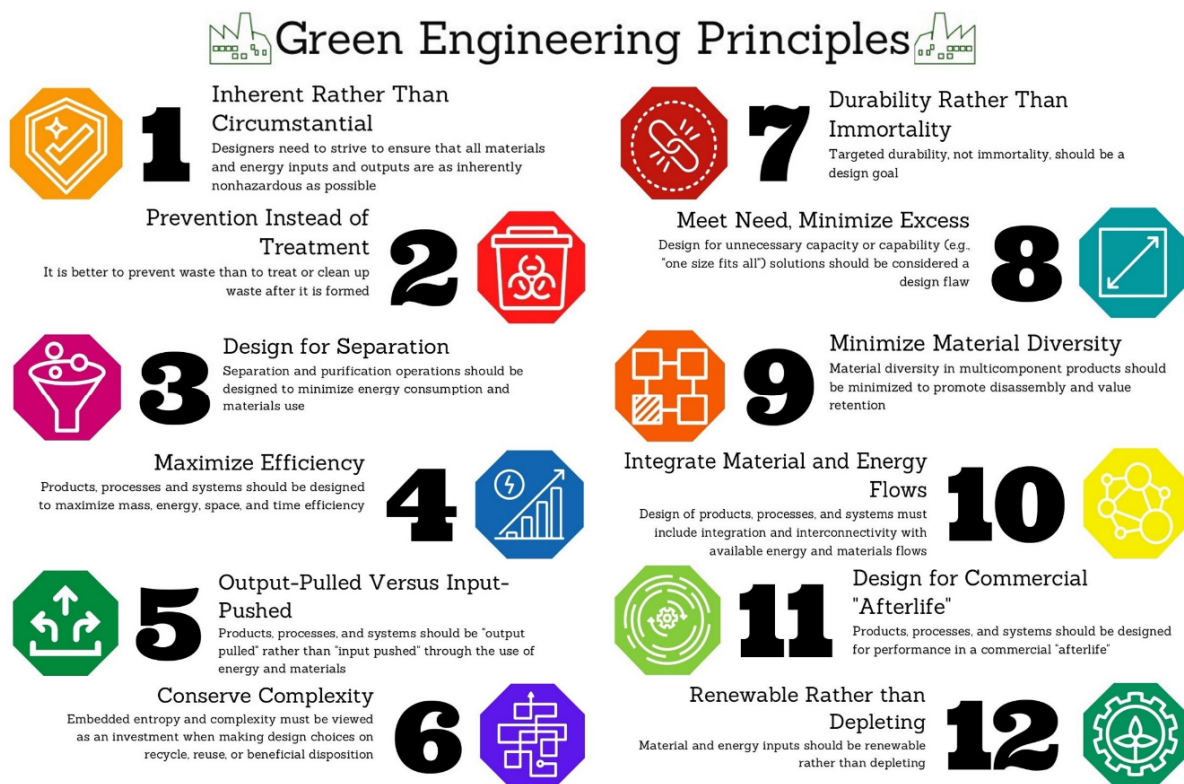


Figure 4. Green Engineering Principles (GEP, with information of [26]).

As mentioned above, heterogeneous photocatalysis prevents wastes instead of treating them (GEP 2). In terms of the degradation of organic pollutants in water, photocatalysis looks for the complete mineralization of the organic matter, transforming complex

molecules into CO₂, H₂O, and other mineral compounds. By achieving this, more reactants are converted to the desired products (minerals) and less in undesired products (potentially toxic intermediates), addressing GEP 2. New photocatalysts are created for using less material to achieve the maximum conversion, such as ultrathin films [42,43], quantum dots, and highly efficient powder catalysts [44]. Additionally, one of the main goals of heterogeneous photocatalysis is to produce sunlight active materials, thus maximizing the mass, energy, space, and time efficiency of the whole process (GEP 4). To design photocatalytic reactors, the maximum utilization of light sources is crucial. Most photocatalytic reactors use electric light sources [45]; in this concern, electric lamps can be replaced by renewable energy harvesting modules, such as solar panels. Heterogeneous photocatalysis has evolved for the last 20 years to minimize energy consumption in separation and purification operations (GEP 3) by the implementation of (a) immobilized photocatalysts (including supported materials and thin films), (b) magnetic materials, and (c) photocatalytic membranes, among other strategies. When the lifetime of photocatalysts is over, some of them can be potential pollutants, flouting GCPs 1 and 4, as well as GEPs 1, 2, and 11. Hence, new photocatalysts should be designed with an afterlife perspective, using non-hazardous materials to encourage their reuse when they are exhausted or designing materials able to be reactivated after several reaction cycles. The latter is especially useful for green H₂ production as cost-effectiveness of the material increases with the number of cycles they can be used without significant performance decreases. Although some metals are abundant on the Earth's crust, others are considered endangered and critical, as shown in Figure 5.

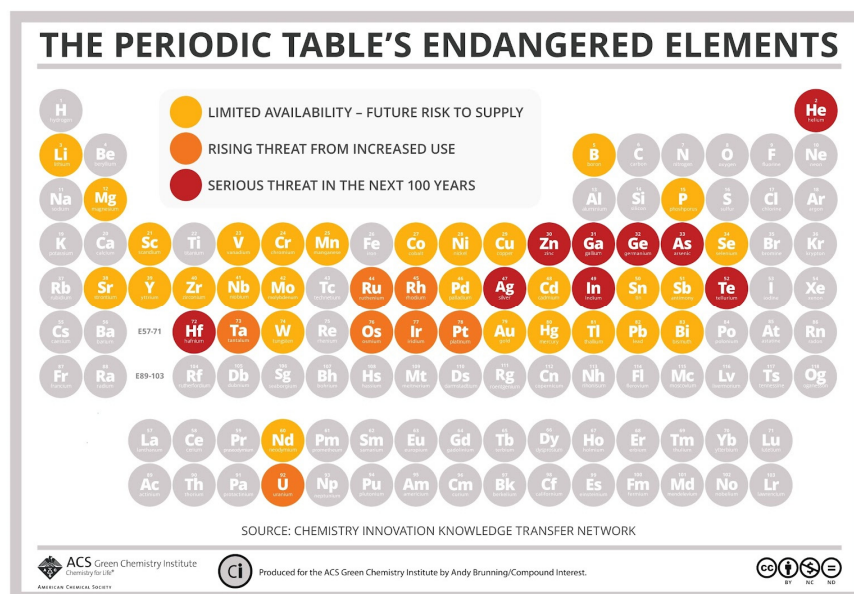


Figure 5. Periodic Table's endangered elements.

The availability and recyclability of raw materials must be considered when designing new photocatalysts for any purposes. For example, Pt is considered as a critical raw material for the European Commission, hence its utilization is restricted despite its outstanding properties as co-catalyst for green H₂ production [46]. The photocatalysts must be designed and synthesized for being recovered after their utilization. Different processes such as solvent extraction, precipitation, ion exchange, crystallization, electrowinning, and electrodeposition are plausible methods for recovery. For example, electrodeposition is a low-cost, scalable, and straightforward method to recover bismuth-based semiconducting materials [47].

Developing new photocatalysts or upscaling the photocatalytic process must be performed following a life cycle perspective, which includes the analysis of the environmental risks carried by the synthesis, the usage, and the disposal of photocatalysts, the effluents produced after water treatment, the emissions from cradle to grave, and the overall upscal-

ing. Life Cycle Analysis also covers the economic sustainability of the process, considering the use of electric energy and the embedded energy costs of consumable chemicals. We consider that integrating Green Principles to the synthesis of new photocatalysts will make room for a new generation of photocatalysts where Life Cycle Analysis will provide a wider picture of the photocatalytic water treatment and green H₂ production systems, causing the process to be more attractive for commercialization. So far, very few works have reported the implementation of Green Principles and Life Cycle Analysis in the development of the green photocatalysis process to shed light on the current bottlenecks to implement these approaches. Therefore, further discussion must be focused on the attempts to upscale heterogeneous photocatalysis from a perspective that includes the Green Principles and Life Cycle Analysis.

3. Upscaling Heterogeneous Photocatalysis for Water Purification and Green H₂ Production

Significant efforts have been undertaken for upscaling the heterogeneous photocatalysis process. The first requirement to achieve this goal is the availability of highly efficient, cost-effective, and stable photocatalysts. In this regard, a plethora of photocatalysts have been tested for the degradation of organic pollutants in water and for green H₂ production since the late 1990s. Metal oxides, such as TiO₂, CeO₂, WO₃, and bismuth-based oxides, are the most used materials (Table 2). TiO₂ is the most popular material in heterogeneous photocatalysis, as it is cheap, innocuous, stable, and highly efficient. However, it is photo-excited under UV light illumination ($\lambda < 380$ nm), which limits its use in solar plants. Different strategies have been implemented to increase the photocatalytic performance of TiO₂ under visible light irradiation, including doping with non-metal atoms and coupling with low bandgap semiconductors [48]. Doping semiconductors results in the formation of inter-band states, reducing the bandgap energy and thus the activation energy. However, it also increases the recombination rate of the charge carriers, which can be managed by the decoration of the semiconductor surface with nanoparticles of noble metals (e.g., Au, Pt, or Pd) [49]. For semiconductor—semiconductor junctions, type-II heterostructures are sought to boost the separation of the charge carriers. In the case of TiO₂ type-II heterostructures with low-bandgap semiconductors, such as WO₃, CdS, CeO₂, bismuth-based, and iron-based oxides are the most reported [50]. Through the aforementioned modifications, different TiO₂-based materials are currently used in sunlight-driven photocatalysis systems, displaying outstanding results [51]. In the case of WO₃, CeO₂, and bismuth-based semiconductors, these materials have lower bandgap values hence they are photoactive under visible light irradiation. However, the recombination of the charge carriers is considerably higher than that of TiO₂, making necessary the modification of these materials. The insertion of inter-band orbitals by doping with non-metal and transition metal atoms is widely used to achieve this. Additionally, the synthesis of secondary and ternary heterostructures to transport the charge carriers from one semiconductor to another is a common way to foster the separation of charge carriers, resulting in highly efficient S- and Z-schemes. Such strategies are detailed reviewed elsewhere [52–54]. Different properties of the metallic oxides should be considered when they are used as photocatalysts. For example, the particle size of WO₃ is normally obtained in ranges near its Bohr radius, which results in quantum confinement effects, such as a blue shift in the bandgap [55]. For tungsten- and bismuth-based materials, photocatalysis under UV light irradiation should be avoided, as these are highly reducible ions that are converted to their metallic state after few reaction cycles.

Table 2. Selected examples of photocatalyst materials commonly synthesized for water treatment and green hydrogen production.

Water Treatment						
Photocatalyst	Model Molecule	Light Source	Reaction Time	Outcomes	Reference	
TiO ₂	TiO ₂ Degussa P-25	Acridine orange and ethidium bromide	Solar light	-	At pH = 10, it achieved the highest degradation rate	[56]
		Organic matter in petroleum wastewater		3 h	At pH = 6.8, the reduction in chemical oxygen demand was of 76%	[57]
	Sol-gel TiO ₂	Rhodamine B	Visible light	3.5 h	60% of degradation rate	[58]
	TiO ₂ /perlite	Furfural	UV light	2 h	99.6% of degradation rate	[59]
	TiO ₂ /cork	Congo red	UV light	2 h	85% of degradation rate	[60]
	TiO ₂ /expanded polystyrene	Drimaren red, indigo carmine, and methylene blue	Solar light	4 h	Almost 100% of degradation rate	[61]
	TiO ₂ /low density polyethylene	Methylene blue	UV light	4 h	35% of degradation rate	[62]
			Solar light		30% of degradation rate	
	TiO ₂ /LECA	Ammonia	Solar light	72 h	96.5% of degradation rate	[63]
	Nano flower-like rutile TiO ₂	Methylene blue	Solar light	3 h	99% of degradation rate	[64]
	Multi-walled carbon nanotube/TiO ₂	2,4-dichlorophenol	UV light	2 h	93% of degradation rate	[65]
			Solar light		87% of degradation rate	
	Bi-doped TiO ₂ nanotubes	Rhodamine B	Solar light	4 h	100% of degradation rate	[66]
	N-doped TiO ₂ nanotubes sintered at 350 °C	Methyl orange	Visible light	4 h	96.3% of degradation rate	[67]
	B,N-codoped TiO ₂ supported on pearlstone	Diesel oil	Visible light	9 h	48% of degradation rate	[68]
		Rhodamine B	Visible light	4 h	89% of degradation rate	[69]
	Fe,N-codoped TiO ₂ /fly ash cenospheres	Rhodamine B	Visible light	1 h	99% of degradation rate	[70]
		Chlorpyrifos		2.5 h	84% of degradation rate	[71]
	TiO ₂	S-triazine herbicides	Visible light	3 h	65% of degradation rate	[72]
	N-doped TiO ₂	Crystal violet dye	UV light	3 h	~100% of degradation rate	[73]
	Ag-TiO ₂ /cork	Rhodamine B	Solar light	4 h	60% of degradation rate	[74]
		Rhodamine B			100% of degradation rate	
	Fe ₃ O ₄ -TiO ₂	Methylene blue	Visible light	1 h	75% of degradation rate	[75]
		Congo red			81% of degradation rate	
	Bi-doped TiO ₂	Methyl orange	UV-visible light	2 h	94% of degradation rate	[76]
	Tb _x O _y -TiO ₂	Phenol	Visible light	3 h	At pH = 4, 100% was degraded	[77]
	Graphene oxide based TiO ₂	2-chlorophenol	Solar light	4 h	80% of degradation rate	[78]
		Bisphenol A	Visible light	3 h	67.6% of degradation rate	[79]

Table 2. Cont.

Water Treatment						
Photocatalyst		Model Molecule	Light Source	Reaction Time	Outcomes	Reference
ZnO	ZnO	RR141 azo dye	UV light	4 h	95% of degradation rate	[80]
		Ofloxacin	UV light	5 h	100% of degradation rate	[81]
	Ag-ZnO	Ofloxacin	Solar light	3.5 h	82% of degradation rate	[82]
	Ag ₃ PO ₄ /ZnO nanowires	Ofloxacin	Solar light	3.5 h	98% of degradation rate	[83]
	MnFe ₂ O ₄ -ZnO	Ofloxacin	UV light	0.5 h	89% of degradation rate	[84]
	ZnO@g-C ₃ N ₄	Congo red	Visible light	3.5 h	54% of degradation rate	[85]
	ZnO-SnO ₂	Sulfamethoxazole	UV light	0.5 h	60% of degradation rate	[86]
	ZnO/C ³⁺ -CeO ₂	Methylene blue	UV light	1 h	95% of degradation rate	[87]
	ZnO-Graphene	Methylene blue	Visible light	6 h	97% of degradation rate	[88]
	ZnO/PANI	Methyl orange	UV light	4 h	96% of degradation rate	[89]
	CeO ₂ -CuO	Methylene blue	UV light	3 h	99% of degradation rate	[90]
	CeO ₂ /g-C ₃ N ₄	Methylene violet	Visible light	1.5 h	93% of degradation rate	[91]
	CeO ₂ /TiO ₂	Sulfamethoxazole	Visible light	1 h	99% of degradation rate	[92]
	CeO ₂	Ag ₂ O/CeO ₂	Tetracycline	Visible light	1.3 h	100% of degradation rate
Ag/CeO ₂		Enrofloxacin	Visible light	2 h	87% of degradation rate	[94]
Pt/CeO ₂ /ZnO		Rose bengal dye	Visible light	3 h	96% of degradation rate	[95]
Co/CeO ₂		Phenol	Visible light	1 h	64% of degradation rate	[96]
Cr/CeO ₂		Methylene blue	Visible light	6 h	96% of degradation rate	[97]
Fe/CeO ₂		Methylene blue	UV light	1.6 h	56% of degradation rate	[98]
Zr/CeO ₂		Methylene blue	Visible light	3 h	97% of degradation rate	[99]
WO ₃	ZnS-WO ₃ -CoFe ₂ O ₄	Methylene blue	Visible light	2.5 h	75% of degradation rate	[100]
	AgBr/WO ₃	Methylene blue	Visible light	3 h	98% of degradation rate	[101]
	WO ₃ /Bi ₂ WO ₆	Rhodamine B	Visible light	2 h	100% of degradation rate	[102]
	BiVO ₄	Salicylic acid	Visible light	6 h	75% of degradation rate	[103]
	BiVO ₄ /TiO ₂ /RGO	Visible light	2 h	52% of degradation rate	[104]	
BiVO ₄	AgI/BiVO ₄	Oxytetracycline	Visible light	2 h	68% of degradation rate	[105]
	Co-Pd/BiVO ₄	Visible light	1 h	80% of degradation rate	[106]	
	BiVO ₄ /P-doped C ₃ N ₄	Phenol	Visible light	3 h	90% of degradation rate	[107]
	RGO-TiO ₂ /BiVO ₄	Tetracycline	Visible light	1 h	97% of degradation rate	[108]
	BiVO ₄ /Bi ₂ S ₃ /MoS ₂	Methylene blue	Visible light	2 h	100% of degradation rate	[109]
	Bi ₂ S ₃ /BiVO ₄	Rhodamine B			97% of degradation rate	
	Ag/Ag ₂ S/BiVO ₄	Methylene blue	Solar light	5 h	93% of degradation rate	
	Malachite green			94% of degradation rate		
	Oxytetracycline	Visible light	16 h	67% of degradation rate	[110]	
		Visible light	2.5 h	100% of degradation rate	[111]	

Table 2. Cont.

Water Treatment						
Photocatalyst	Model Molecule	Light Source	Reaction Time	Outcomes	Reference	
Green hydrogen production through the water splitting reaction						
Photocatalyst	Sacrificial agent	Light source	Reaction time	Outcomes	Reference	
TiO ₂	Mesoporous N-TiO ₂ calcined at 250 °C	Methanol (25% <i>v/v</i>)	Visible light	5 h	31.5 µmol h ⁻¹ g ⁻¹	[112]
	Core shelled N-TiO _{2-x}	Methanol (20% <i>v/v</i>)	Sunlight	3.5 h	15 mmol h ⁻¹ g ⁻¹	[113]
	Pt/N-TiO ₂	Formic acid (10 ⁻³ mol L ⁻¹)	Visible light	6.5 h	50.46 µmol h ⁻¹ g ⁻¹	[114]
	Ag/TiO ₂	Ethanol	UV and visible light	6 h	1.34 µmol h ⁻¹ cm ⁻²	[115]
	Ag/Ce-TiO ₂	Ethanol (10% <i>v/v</i>)	UV and visible light	6 h	1.47 mmol h ⁻¹ cm ⁻²	[116]
	Fe,Ni-doped TiO ₂	Ethanol (95% <i>v/v</i>)	UV and visible light	4 h	24.3 mmol h ⁻¹ g ⁻¹	[117]
	Fe-doped and Cr-doped TiO ₂ thin films	-	Visible light	6 h	15.5 µmol h ⁻¹ cm ⁻²	[118]
	Co-doped TiO ₂	Glycerol (5% <i>v/v</i>)	UV and solar light	10 h	11,021 µmol h ⁻¹ g ⁻¹	[119]

Photocatalytic reactors have been developed and tested for many years, using several configurations and materials. Different optimization strategies have been used to increase the efficiency of these systems at higher scales. Reactor configuration/geometry is a crucial factor to be considered when upscaling at microplant, pilot plant, or industrial levels [120–122]. Additionally, optimizing the operational parameters of the reactor can be performed using the desirability function method, which helps to achieve the efficient target response proportional to the efficiency of the upscaled system [123].

In laboratory and higher scale reaction systems, the photocatalyst is present either suspended, supported on inert particles, or as thin films; for the latter, the photocatalyst can be supported on glass, quartz, ceramics, or metallic substrates [124]. Glass is regularly used as substrate for thin films, while metallic substrates, such as stainless steel, are preferred for full-scale processes as they can cope with high mechanical stress and are inert to the reactive species produced upon the irradiation of the semiconductor [124]. On the other hand, plastic materials, such as polythene, poly acrylate, or PVC tubes are also used as substrates of thin films as they are flexible and cheap [123,125]. However, polymers can be etched by the reactive oxygen species, releasing the catalyst to the aqueous phase. This drawback can be addressed by coating the polymeric substrate with an inert layer, such as SiO₂ [126]. Supporting the photocatalyst facilitates the recovery of the material to further reaction cycles, in the case of batch systems, or allows for a continuous process in H₂ evolution. Removing the unitary operation to recover the catalyst leads to a more efficient use of energy, which is in line with GEP 3. However, when the photocatalyst is supported, a considerable fraction of the surface area is lost due to the agglomeration of the particles on the support, resulting in a drop of the reaction efficiency. The synthesis of photocatalytic thin films requires the deliberately production of material in excess, which is a flaw in accordance with GEP 8. Recent research has focused on the development of ultrathin films supported on different substrates, aiming at increasing the efficiency in material usage to achieve high performances in the removal of organic pollutants from water and the water splitting using less material [42,127]. Even when the immobilization of the photocatalyst can provide advantages, slurry reactors are preferred in research laboratories and mild-scale plants [128] for practical and cost-effective reasons. According to the perspective study of Toe et al. [129], a photocatalytic slurry system is nearly 12% more cost-effective compared to a panel photoreactor to produce green H₂ under the case scenario of producing 10 kg H₂ per day. In addition, slurry photoreactors provide better light penetration and scattering, superior mass transference, and easier installation and maintenance compared to photoreactors where the catalyst is deposited as thin films [128,129]. Conversely, using an excess of the powder photocatalyst leads to the decrease in the reaction performance because of over light scattering, causing a reduction in the quantum efficiency [130], light screening effects, and increased costs associated with the separation of the solid material. The latter is a crucial step in water treatment systems, as the remaining particles of the photocatalyst impact the quality of the effluent, especially when the semiconductor is made up by toxic elements, such as Cd, Pb, or some halides. The catalyst recovery can be performed using membranes that act as filters for the further retrieval of the solid. On the other hand, the photocatalyst can be supported on the membranes, resulting in reactive photocatalytic filters for the degradation of contaminants. In this scheme, the filtration cake formed through the process is simultaneously degraded with the dissolved contaminants [64,131]. The utilization of photocatalytic membranes and thin films synthesized by different chemical methods (e.g., dip coating, chemical vapor deposition, pulsed laser deposition, and ultrasound process) are mostly preferred over slurry photoreactors at microplant or industrial scales [128–130]. However, they are yet to be commercially established due to the difficulty of immobilizing the nanomaterials over large surfaces [132]. For green H₂ production, the recovery of the catalyst is not necessary as the photocatalytic system is kept functioning as much as possible while the main gaseous products are recovered at the upper part of the reactor. Contrary to the definition, photocatalysts normally deteriorate as they are reused due to (a) poisoning with dissolved minerals, (b) photo-corrosion, and (c) solvation.

Hence, powder and immobilized photocatalysts must be highly reusable to be considered as cost-effective materials in heterogeneous photocatalysis. According to Uekert et al. [133], a lifetime of at least one year is essential for a photocatalyst to be considered for practical application at higher scale.

So far, different reactors have been tested for upscaling purposes. The parabolic trough concentrator (PTC) was the first reactor for sunlight-driven photocatalytic water treatment [134]. Even though it has the advantages of harvesting sunlight and high mass transfer, the heating in the system is a disadvantage that may diminish the process efficiency, given that the adsorption of organic molecules on the catalyst decreases as the temperature rises. Additionally, their apertures collect only the direct incident rays, which may question the practicality of the PTCs in various climatic conditions [134]. The implementation of sun tracking systems increases the performance of the photocatalytic process, raising the prices of the whole system. Later, non-concentrating collectors (NCC), without the necessity of tracking systems, were introduced [128]. Flat plate collectors are typically used in NCCs, on which the catalyst is supported, and the liquid phase reaction mixture is directly in contact with the support before it reaches the catalyst. The NCCs are cost-effective and function in all climatic conditions as they use the sunlight beam from all directions and the tracking system is unnecessary, causing the system to be cost-effective. Compound parabolic concentrators (CPCs) are the next generation of photoreactors, combining NCC and PTC advantages. CPCs are alternatives to the reactors with the tracking system as they can collect both direct and indirect radiation due to their architecture, being an energy-saving type depending on the availability of sunlight irradiation [135]. Non-collecting reactors, such as tubular, shallow ponds, and falling film reactors have been utilized for photocatalytic water treatment [128,134,136]. Reactors using lamps as light sources have also been tested, with annular reactors as an example, and systems with lamps around the reactor chamber instead of inside [134]. So far, these systems are limited to pilot and demonstration-scale plants [128]. Overall, the upscaling process has been a challenge compared to the development of new photocatalysts (see Figure 2). This trend of being in the comfort zone of laboratory-scale synthesis and applications must be changed to boost the application of material science and thus develop the technology for upscaling photoreactors looking for the best conditions and further commercialization.

Selected Upscaling Case Studies

Upscaled photocatalytic systems have been tested mostly for water treatment worldwide. The distribution of this kind of treatment plants mainly depends on the ambient conditions, with sunlight irradiation being the most important parameter. Many of the upscaled systems are in the sunbelt region, in locations such as Tabernas in Spain, Arica in Chile, and Doha in Qatar. Some other sites, such as the Sonora and Atacama deserts, Sub-Saharan Africa, and West Australia reportedly have higher photovoltaic power potential and global horizontal sunlight irradiation (Figure 6), with a great potential for testing photocatalytic plants. Upscaled photocatalytic reactors located in high sunlight irradiation regions are greatly effective, although the economic and design parameters vary considering the inter-day and seasonal oscillations of sunlight irradiation [137].

In the National Renewable Energy Laboratory (Albuquerque, USA), six aligned PTCs were tested. The devices were modified with a UV-light transparent pipe and the reactors were irradiated with sunlight concentrated 50 times. The light reached the 450 m² parabolic collector using a movable collector aperture perpendicular to the incident sunlight and the reflected rays were concentrated to an absorber tube aligned to the parabolic concentrator. Using this device, it was demonstrated that 1,2,3,4-tetrachloro-*p*-dibenzodioxin can be photocatalytically degraded using the full solar spectrum, compared to that observed when the 450 nm cutoff filter was adapted. This was the first attempt toward an upscaled photocatalytic system and the first known outdoor plant [138]. Other PTCs were reportedly installed at the Lawrence Livermore National Laboratory (Livermore, CA, USA) to treat groundwater contaminated with trichloroethylene, using a TiO₂-based solar plant [139]. In

this 158 m² parabolic concentrator, 570 L of groundwater were irradiated with an effective sunlight concentration ratio of approximately 20, achieving a degradation yield of 90% in single pass experiments at neutral pH. The reaction efficiency increased to 100% under acidic conditions (pH = 5.6). The optimal concentration of TiO₂ in the slurry reactor was 1 mg L⁻¹, while increasing the flow rate marginally improved the degradation of trichloroethylene.

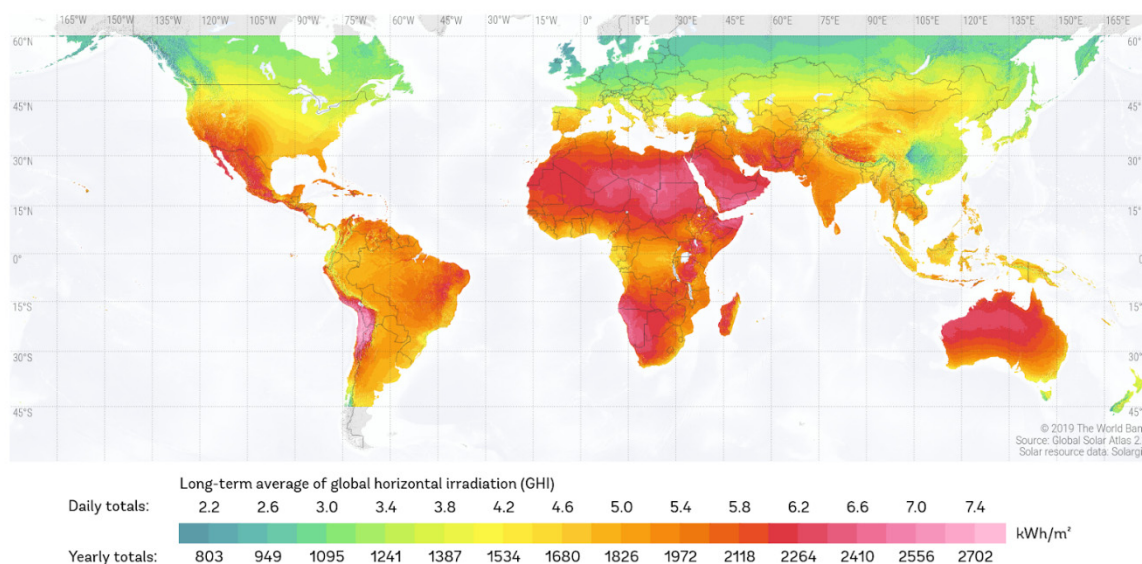


Figure 6. Global horizontal irradiation (Global Solar Atlas).

In the *Plataforma Solar de Almería*, Spain, some PTCs were built to detoxify water. The consortium of six parabolic modules was designed to treat up to 419 L of water, at flow rates from 250 to 3500 L h⁻¹, which has been the first engineering-scale solar photochemical facility in Europe for such a purpose [140]. Most recently, a Non-Concentrating Collector (NCC), consisting of a rectangular staircase vessel with 21 steps, covered by a Pyrex glass screen to avoid evaporation, was also tested to remove 4-chlorophenol from water (Figure 7). Commercially available TiO₂ was coated on non-woven paper using SiO₂ as a binder agent and the surface-modified sheets were deposited on the steps of the photoreactor [141]. Different experiments were performed to treat a maximum volume of 35 L of wastewater effluent. The complete degradation of the target molecules was achieved upon 5 h of sunlight irradiation at a flow rate in the range from 1 to 7.5 L min⁻¹, although the mineralization yield was below 100%. Still, the conversion achieved using the non-concentrating collector was slightly higher than that attained with a compound parabolic collector. Moreover, the detoxification of water containing the Congo red and indigo carmine dyes was reported in terms of the degradation of the molecules and their mineralization. This was one of the first reaction schemes demonstrating that supported photocatalysts can efficiently remove organic pollutants in water, avoiding the unitary operation of separating the solid from the liquid phase.

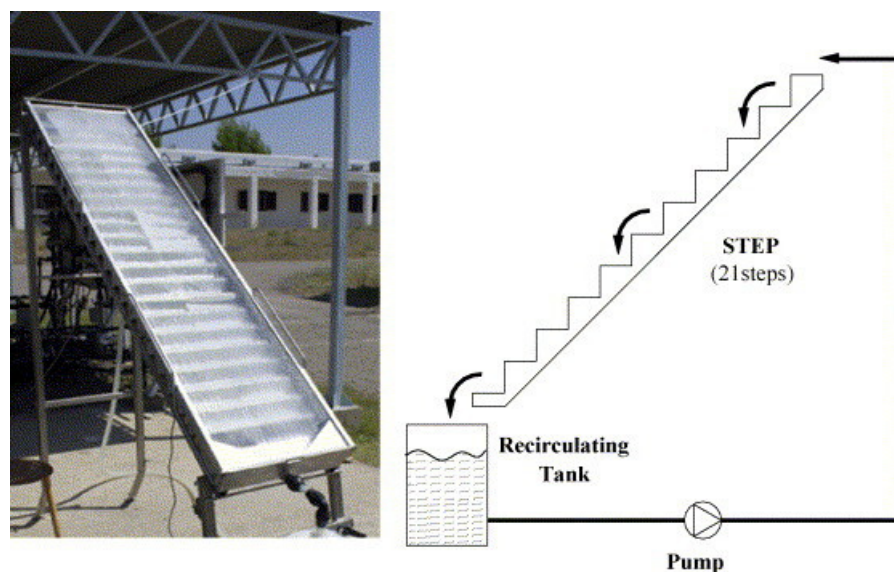


Figure 7. Non-concentrating solar collector tested at the *Plataforma Solar de Almería*, Spain (reproduced with permission of [141]).

In recent years, different efforts to harness the abundant sunlight irradiation in Spain have been performed. For example, a flow-through reactor using stainless steel wires to support nanosized ZnO was tested at the *Instituto Nacional del Carbón* to remove methylene blue (10 mg L^{-1}) from water using UV irradiation [142]. In laboratory scale experiments, a flow of 20 mL h^{-1} were passed through the photocatalytic mesh as the UV light source ($300\text{--}400 \text{ nm}$, 10 mW cm^{-2}) was 26.6 cm above. From 50 to 60% of the methylene blue was degraded after 3 h of irradiation, depending on the amount of ZnO deposited. On the other hand, the mineralization was modest, from 20 to 30% after 17 h of irradiation. Some release of ZnO from the stainless-steel mesh was observed, necessitating an increase in the adherence of the semiconductor to the support to avoid posing risks on the aquatic organisms receiving the effluents when this system is scaled.

The SOWARLA demonstration plant at the German Aerospace Center is planned to be capable of purifying water polluted with rocket fuels (some of them containing cyanide, nitrite, and hydrazine derivatives) using a new configured solar reactor, with a cost five times lower than a conventional UV-light harvesting reactor (Figure 8) [143–145].

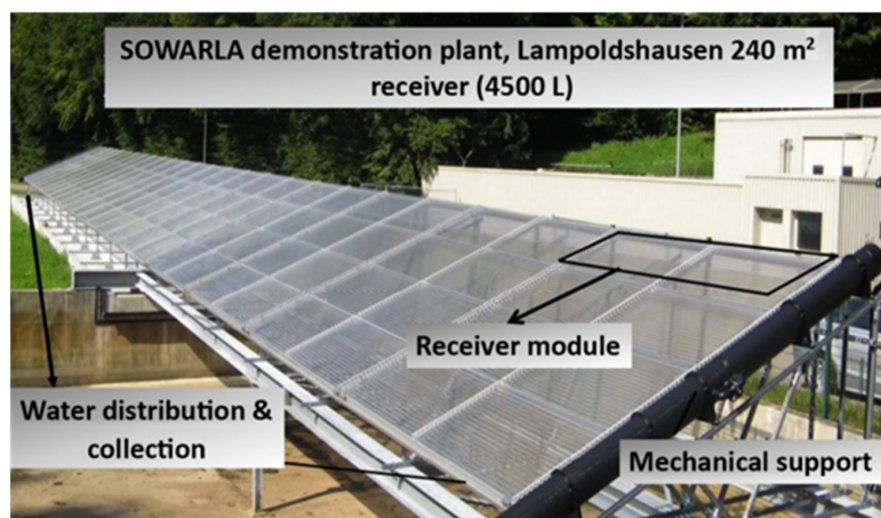


Figure 8. The SOWARLA demonstration plant, (taken with permission from [143]).

A prominent example of an industrial scale photocatalysis plant to treat water using compound parabolic concentrator is SOLARDETOX, which was developed by the European Industrial Solar Consortium. With a parabolic mirror and a series of Pyrex tubes, the plant collects irradiation over 100–150 m² to treat large volumes of water using TiO₂ to remove dichloroacetic acid and cyanide [139,146]. Unfortunately, this technology has not been used to treat real wastewater streams yet.

In the United States of America, a pilot-scale photocatalytic membrane reactor (PMR) was used to remove 32 endocrine disrupting compounds at ng L⁻¹ levels in water from the Colorado River. This patented configuration uses UV/TiO₂ photocatalysis, followed by filtration through a ceramic microfiltration membrane to recover and recycle the photocatalyst [147]. In this reactor, 50 mg L⁻¹ of the photocatalyst was exposed to UV light ($\lambda = 185$ and 254 nm) from a set of 32 lamps through very short timespans (below 30 s), at a flowrate of 24 L min⁻¹. Steroid hormones were completely removed from water, along with most of the tested pharmaceuticals, including diclofenac, sulfamethoxazole, and fluoxetine, while flame retardants, especially perfluorooctanesulfonic acid, remained in the water.

The PMR technology has also been used in the Planta Solar de Almería, which was adapted to a compound parabolic concentrator using a TiO₂ P25 suspension (0.2 g L⁻¹) to remove lincomycin (from 10 to 50 μ mol L⁻¹) in 40 L of water at a flow rate of 10 mL s⁻¹ and displaying promising results. The system can be used either as a batch or continuous reactor, finding the complete degradation and high mineralization of the antibiotic regardless of its initial concentration [148]. The use of membranes in the system significantly reduced the presence of degradation byproducts and photocatalyst in the effluent, resulting in a safer process.

In Japan, a Rotating Advanced Oxidation contactor (RAOC) using TiO₂ supported on zeolite particles was used to remove sulfonamide pharmaceuticals from water (Figure 9). A zeolite/TiO₂ composite sheet was attached to a rotating wheel and researchers were able to remove up to 96% of sulfamonomethoxine after 180 min under UV-light irradiation [149,150].

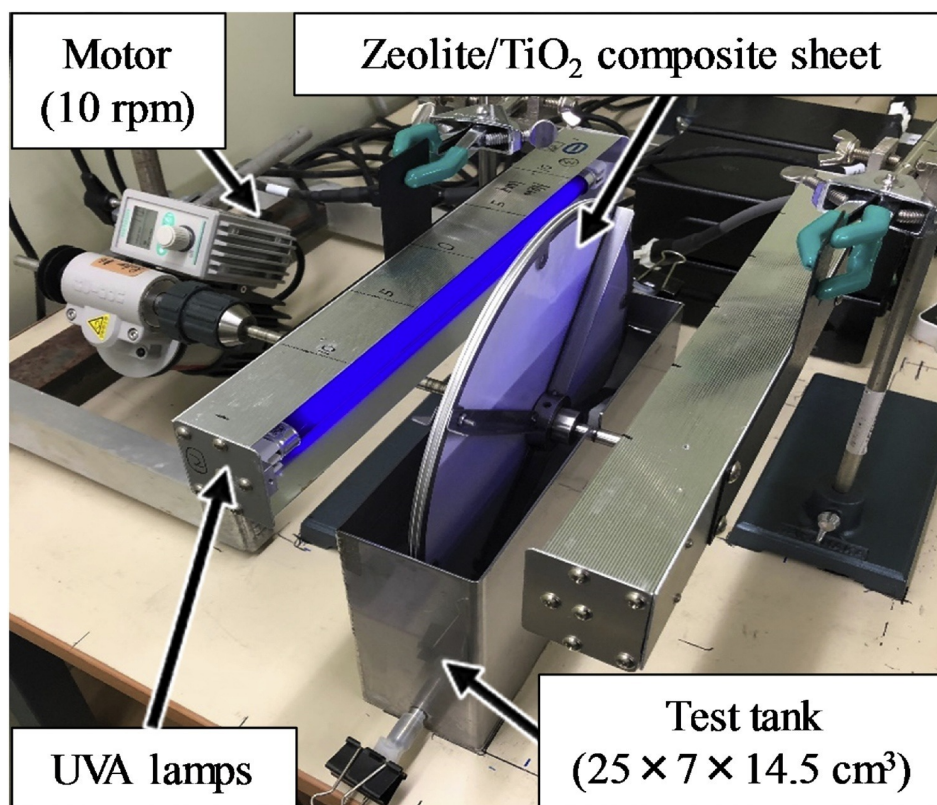


Figure 9. Rotating advanced oxidation contactor (RAOC) equipped with zeolite/TiO₂ composite sheets (reproduced with permission of [150]).

A reactor functioning with solar batteries and a $\text{Bi}_2\text{O}_3/\text{TiO}_2$ thin film as photocatalyst was used to purify 40 L of wastewater from aquaculture effluents in China. The photocatalyst was able to degrade organic nitrogen compounds from water using sunlight irradiation (from 55 to 70 mW cm^{-2}) and, during the night, UV light lamps ($\lambda = 254 \text{ nm}$) were activated using batteries. After 24 h of water recirculation, the organic nitrogen compounds were removed, while the content of NH_4^+ and NO_3^- decreased by 30% and 50%, respectively [151]. In the same line, a pilot-scale Thin-Film Fixed-Bed Reactor (TFFBR) was tested to inactivate the aquaculture pathogen *Aeromonas hydrophila* under sunlight irradiation, using a sloping flat plate coated with TiO_2 as the photocatalyst. In this homemade system, 200 mL of water was in contact with a thin film of the photocatalyst (20.5 g m^{-2}) and exposed to sunlight for 2.5 min. At a flowrate of 4.8 L h^{-1} , the inactivation of 1.3 log units of bacterial cells was achieved in a single pass of spring water through the reactive bed. The bacterial cells displayed injuries due to the attack of the reactive oxygen species [152].

In the African continent, the effluent from a textile factory in Menzel Temime (Tunisia) was treated in a solar pilot plant with two Flow Film Reactors (FFR), with an illuminated surface area of 50 m^2 and a photonic efficiency of 15%. This reactor was designed for treating up to $1 \text{ m}^3 \text{ h}^{-1}$ of effluent and removing recalcitrant contaminants, such as dichloroacetic acid. This scheme was chosen considering the low investment costs and energy consumption requirements [153]. According to the authors, high removal of chemical oxygen demand and total organic carbon was achieved after few reaction cycles under sunlight irradiation. The optimized scheme was planned to remove an average of $405 \text{ mg of carbon h}^{-1} \text{ m}^2$. Unfortunately, no reports on the functioning of this plant were found beyond 2004.

The Ramadan City in Egypt, which has many industries and obtains sunlight almost all over the year, has been recently equipped with semi-industrial constant flow photovoltaic reactors that utilize the direct sunlight irradiation to purify treated wastewater. Nanocomposites comprised by $\text{SiO}_2/\text{TiO}_2$ (2:1) supported on polymeric membranes were used as photocatalysts to degrade methyl orange and phenol (10 mg L^{-1} , each one) as model molecules. Degradation rates of 54% and 41% were obtained for phenol and methyl orange, respectively, after 3 h under autumn sunlight irradiation (868 W m^{-2}) [154]. According to the authors, using this system lowers the operation costs of treating $0.5 \text{ m}^3 \text{ d}^{-1}$ of water to a third of the cost of a small photoreactor using electricity. On the other hand, in Alexandria, Egypt, where the sewage water is deposited mainly through public sewers, a homemade CPC was proposed to treat industrial effluents. In this system, TiO_2 was deposited on recycled polymeric substrates (cotton, polyamide, and PET, among others) and tested to remove acid yellow 28 and methylene blue (5 mg L^{-1} each one) as well as chemical oxygen demand. In this scaled system, 3 L of wastewater effluent were pumped at a flow rate of 1.2 L min^{-1} and sunlight was irradiated (2.74 mW cm^{-2}) all day long, starting at 9:00 AM. The complete degradation of both dyes was achieved after 8 h of irradiation using TiO_2 supported on PET; however, the performance of the photocatalyst dropped with the reuse, most likely due to the affectation of the polymeric substrate [155].

Regarding the production of green H_2 , Schroder et al. [156] made the first attempt at a large-scale with water splitting photoreactors using natural sunlight, graphitic carbon nitride as photocatalyst, and triethanolamine as the sacrificial agent. The authors reported producing around 18 L of green H_2 in one month at a hydrogen evolution reaction rate of 0.22 L kW h^{-1} and a maximum solar-to-hydrogen conversion of 0.12%. In another study, Maldonado et al. [157] proposed a pilot-scale solar photoreactor with 2.6% conversion efficiency using Cu/TiO_2 as the photocatalyst. The system was tested using different aqueous matrices, such as water/methanol, water/glycerol, and wastewater effluents. Glycerol was the best sacrificial agent, while the poorest yields were obtained using wastewater, due to the complexity of the matrix and the hydrogen–oxygen back reaction [157]. Villa et al. [158] compared the performance of $\text{Pt}/\text{N-TiO}_2$ and $\text{Pt}/\text{CdS-ZnS}$ in a pilot-scale plant (25 L of capacity) for water splitting, using formic acid and organic matter in municipal wastewater as sacrificial agents. Moderate conversions were obtained

using wastewater, highlighting the possibility of valorization of this waste as raw material to produce green hydrogen. After 5 h of sunlight irradiation, around $3000 \mu\text{mol L}^{-1}$ of H_2 was produced using 0.2 g L^{-1} of platinized N-TiO₂ and formic acid as the sacrificial agent. The yield dropped to $220 \mu\text{mol L}^{-1}$ when the photocatalytic process was performed using wastewater and 5 g of Pt/(CdS-ZnS) as the catalyst. Overall, the conversion efficiencies were 2.5% for Pt/N-TiO₂ and 1.6% using the Pt/(CdS-ZnS) material. Almomani et al. [159] tested a solar pilot plant using carbon-doped TiO₂ nanotubes as the photocatalyst under sunlight irradiation. Using 50 mg of the photocatalyst, the average rate of hydrogen production was $38.66 \text{ mmol h}^{-1} \text{ g}^{-1}$ through 50 h of sunlight irradiation, which is 1.5 times higher than the maximum rate reported for other TiO₂-based photocatalysts at a lower scale so far. Ren et al. [160] tested a CPC-based photocatalytic reactor for water splitting, with a volume of 11.4 L , having a maximum hydrogen production of 1.88 L h^{-1} under direct solar irradiation.

In the *Plataforma Solar de Almería*, Arzate-Salgado et al. [161] used the Au/TiO₂ photocatalyst to simultaneously produce hydrogen and degrade organic pollutants in aqueous solutions under sunlight irradiation at bench scale (27 L of capacity at a flow rate of 20 L min^{-1}). Using a catalyst loading of 0.2 g L^{-1} , the authors obtained $6.5 \text{ mmol H}_2 \text{ L}^{-1}$ after 5 h of irradiation and a STH conversion efficiency of 1.8%. Even when formic acid demonstrated to be the most efficient sacrificial agent, dissolved organic matter displayed a positive effect on the photocatalytic water splitting process.

In 2018, the State Key Laboratory of Multiphase Flow in Power Engineering from the Xi'an Jiaotong University built a pilot-scale system based on CPC reactors (3.6 m^2 in area and 23 L in volume). A sodium sulfate solution was used as the liquid matrix and $\text{Cd}_{(1-x)}\text{Zn}_x\text{S}$ was the catalyst in the slurry reactor, at a loading of 2.77 g L^{-1} and a linear velocity of 1.2 m s^{-1} . The average hydrogen production of $184.3 \text{ mL min}^{-1}$ was achieved when the average solar radiation was 803.8 W m^{-2} [162].

Most recently, in 2021, Nishiyama et al. [163] built a 100 m^2 -scale plant for the photocatalytic water splitting. It consisted of 1600 reactor units and a gas separation facility, using $\text{SrTiO}_3\text{:Al}$ as the photocatalyst. The active volume of the system was 2.4 L . According to the authors, the system reached a STH of 0.76% and was operated during a year under field conditions with no incidents. Still, the STH conversion rate should be from 5 to 10% to ensure the systems are economically viable, meaning much work to improve the efficiency remains ahead.

4. The Foreseen Challenges in Upscaling the Heterogeneous Photocatalysis Process for Green H₂ Production

Most of the reported research covers the topics related to heterogeneous photocatalysis for water treatment, while less reports are on the upscaled green H₂ production via the water splitting reaction. In our opinion, this is the result of (a) the lack of effective and durable photocatalysts for the water splitting reaction; (b) the complex experimental setups that are hardly scalable; (c) the safety measures necessary to work with H₂; (d) the challenges related to H₂ storage; and (e) the difficulties of handling and distributing H₂ from plants to the final consumer. As mentioned above, the photocatalysts used for water splitting must have a reduction potential in the conduction band higher than that necessary for the reduction in H^+ into H₂. A limited number of metallic oxides meet this condition and, therefore, surface modified oxides are used. For example, TiO₂ and WO₃ are modified with noble metal nanoparticles to reduce the recombination of charge carriers and slightly increase the reduction potential of the photo-electrons. This leads to highly effective photocatalysts [55,164]; however, the decoration with noble metal nanoparticles increases the costs of the materials and promotes the use of hazardous reagents, such as ethylenediamine. Bismuth-based semiconductors are promising materials for H₂ production due to their highly reductive conduction band and the low oxidation potential of the valence band [165,166]; the latter opens the possibility of high conversion with no addition of sacrificial agent. WO₃ and bismuth-based semiconductors are used in

heterostructures with TiO_2 for H_2 production under visible light irradiation [167]. However, both oxides are readily reducible hence lowering their durability as photocatalysts under reductive conditions. When other calcogenides, such as sulfides or selenides are used, photocorrosion significantly reduces the durability of the materials, as occurs with CdS and Bi_2S_3 . The synthesis of semiconductor—semiconductor heterostructures, removing oxygen from the photocatalytic system and decoration with noble metal nanoparticles are strategies to increase the lifetime of these photocatalysts by inhibiting photocorrosion [168]. Multiple efforts must be performed to obtain durable photocatalysts for green H_2 production using synthesis processes that meet the Green Principles. The typical laboratory scale setup for the photocatalytic production of green H_2 consists of a tightly sealed glass reactor, the light source, a continuous stirring system, and the gas purge. Batch configuration is mainly used, where the reagents and the catalyst are introduced into the reactor after the air is purged. The efficiencies obtained at this scale do not necessarily apply to the upscaled system. Incorporating the optimized conditions obtained at lab-scale to the upscaled system is of high importance. Homogeneity of the reaction medium is an essential factor in the upscaled systems either using slurry reactors or immobilized catalysts, which is possible through an efficient stirring system. Palette mixing systems for low-density materials and flotation to maintain a homogeneous loading of denser solids are options in this concern. In scaled systems, the light source must cover the whole surface of the reactor and guarantee the maximum number of photons reaching the bottom of the reactor to avoid poorly illuminated spots. To accomplish this, high-power lamps can be used, with the consequent increase in the reaction temperature; in such a case, a circulating cooling system is necessary to dissipate the heat. Even though immobilization is an efficient solution to reduce the complexity of the process, the fouling of the immobilized catalysts may be an issue that further affects the efficiency of the system [169].

Boiling point, ignition temperature and energy, density and permeability for different materials, high diffusion coefficient in air, and latent heat of combustion cause hydrogen to be an excellent fuel. To use this product to supply clean energy, it is necessary to consider the risks of leakage, ignition, and explosion. Hydrogen embrittlement consists of the exposition of metallic and plastic liners to H_2 , which may change their mechanical properties, resulting in cracks and blisters on pressurized vessels and pipelines. Leakage is hardly detected since hydrogen is colorless, odorless, and tasteless [170]. The leakage of gaseous H_2 in closed spaces can cause asphyxia even at low concentrations, as it replaces the oxygen, while in both open and close spaces it may cause explosions. An initial explosion or jet fire can trigger a domino effect with nearby vessels by thermal radiation, resulting in subsequent fireballs or another jet fire. In the case of liquid H_2 , the main problem is the change of pressure necessary to liquefy the gas; the difference in temperature of liquid H_2 and the outside evaporates the released fuel in complete or partial form. When total vaporization of the fuel occurs, it mixes with air creating a flammable cloud. In contrast, in partial vaporization, a cryogenic pool is formed on the ground surface, absorbing heat from both the atmosphere and the ground to create a boiling film while the freezing of the solid occurs followed by the condensation or freezing of the surrounding air [171]. To avoid hydrogen embrittlement, extensive research is going on over the materials of the pipes and tanks for synthesis and storage purposes to improve the reactors and devices.

Leakage of liquid H_2 can cause a Boiling Liquid Expanding Vapor Explosion (BLEVE) as the leak changes the inner pressure of the H_2 vessel, thus generating an expansion of the liquid and vapor phases. This causes the rupture of the vessel at atmospheric pressure and under temperature above the boiling point of the gas, which immediately turns into an expansive wave of vapor. An example of a BLEVE event and its potential consequences occurred in the San Juan Ixhuatepec explosions in Mexico in 1984. The gas plant was destroyed and over 500 persons were killed, 7000 had injuries, and nearly 60,000 people were evacuated; 149 houses were completely destroyed [172].

In terms of H_2 storage, chemical and physical sorption have been studied as alternatives to store this green fuel. Some materials, such as MOFs and carbon porous materials

have been studied with promising results. On the other hand, the formation of metallic hydrides allows for storage at low temperatures and pressure. The most widely tested metal hydrides are sodium alanate, lithium imide, and lithium and sodium borohydride [173]. Some of the challenges related to chemical sorption are costs, difficulties handling the storing material, and the occurrence of unwanted gases during desorption. A significant challenge is how H_2 production and storage can meet the GCPs and GEPs (especially GCP 5 and 12 and GEP 1 and 2). The risks of leakage, ignition, and explosion in storage cylinders can be reduced through the implementation of different measures, such as (a) improving the design with materials resistant to embrittlement, and (b) using safety devices, such as Thermal activated Pressure Relief Devices (TPRD) [174].

5. Automation and Machine Learning as Powerful Tools to Upscale Heterogeneous Photocatalysis following the Green Principles

Automatization refers to the creation and application of a wide range of technological approaches to monitor and control the production and delivery of products with lower human intervention, increasing the precision of the process and also the massive production [175]. In the field of heterogeneous photocatalysis, automation is mostly used at the laboratory scale to (a) accelerate the synthesis and characterization of new photocatalysts and (b) the in situ or in operando monitoring of the photocatalytic reaction [176,177]. So far, automation is reported in the literature for the control of valves in green H_2 production devices [178,179], the implementation of Cartesian robots in high-throughput synthesis, characterization and reaction schemes [180,181], and the generation and implementation of flexible automation tools working on lab benches to synthesize photocatalysts for green H_2 production under optimal conditions [182] (Figure 10). Until 2020, the use of industrial robots in materials research laboratories was limited because of the high costs, safety issues, and the necessity of highly specialized personnel for control. However, this situation has been reverted with the drop of the costs of highly specialized robots [183].



Figure 10. Chemist robot at laboratory scale used for the synthesis of photocatalysts to produce green H_2 [182].

Through the automation of the synthesis and reaction processes, data sets are rapidly generated (data mining) and analyzed to achieve the best possible synthesis and reaction conditions and further upscale the photocatalytic systems. Automation is seen as one of the bricks to build scaled photocatalysis plants and it is currently used in the first large-scale photocatalytic solar H₂ production plant for the control of valves and pumps as well as to monitor the water level in the reactor [163]. On the other hand, high-throughput methods in conjunction with machine learning boost the discovery of highly active photocatalysts for solar energy application [184]. Through these approaches, some of the Green Principles can be addressed in the synthesis and characterization of new or improved photocatalysts. In this section, the applications of automation, high-through methods, and machine learning applied to heterogeneous photocatalysis are revised on the basis of their contributions to upscale the process by complying to as many Green Principles as possible.

5.1. High-Throughput Methods for the Discovery of New Photocatalysts at Laboratory Scale

High-throughput or combinatorial methods have been widely used in chemistry since the 20th century to create new bioactive molecules from a wide range of precursors [185]. In the late 1990s, high-throughput methods started to be used to discover new photocatalysts by obtaining libraries of semiconductors. These libraries were constituted of different compositions of semiconductors, including heterostructures, for screening studies aimed at finding the optimal compositions to be used in heterogeneous photocatalysis [186]. Sol-gel and solvothermal routes have been the most commonly used synthesis methods to obtain powders in high-throughput schemes, due to their simplicity, low cost, and fine control of the morphology and architecture of the obtained nanoparticles [187,188]. Several automated devices are currently available to parallelly synthesize and characterize powder semiconductors at the laboratory scale [189]. On the other hand, research on the synthesis of thin films through combinatorial methods has been more prolifically explored in the last two decades, implementing the automation for the synthesis and characterization of photocatalysts to produce green H₂. For example, Kumari et al. [190] used combinatorial reactive magnetron cosputtering methods to synthesize three libraries (342 materials each one) of Fe-V-O thin films. By the variation of the composition and thickness of the films, the highest efficiency for the solar water splitting was achieved with the FeVO₄ phase and a Fe composition from 54 to 66 at.%, finding no effects from the film thickness. More recently, the libraries of vanadate-based semiconductors were expanded using other metals, including Cu, Ag, W, Cr, and Co [191]. Different research groups worldwide have adapted their devices to parallelly synthesize wide libraries of thin film photocatalysts, in most cases using robotized procedures to significantly reduce the time consumption of the synthesis and characterization steps while maximizing the accuracy [192]. High-throughput synthesis at the inter-laboratory level has been developed to boost collaborative—and remote—work that adds new information for data mining to rapidly discover new photocatalysts while fostering the independent corroboration of the information generated in other research groups. In this regard, Hattrick-Simpers [193] reported high reproducibility across different laboratories for the synthesis of Zn-Sn-Ti-O thin films via high-throughput methods based on combinatorial physical vapor deposition (cosputtering and pulsed laser deposition). High-throughput methods can be also applied for the synthesis of micro-photoreactors, which have proven to efficiently increase the photocatalytic performance compared to some thin films, providing advantageous fast retrieval of the catalyst from the aqueous phase [194–196]. Research groups worldwide have proven the efficiency of continuous flow and immobilized microfluidic-based photo-reactors to degrade organic pollutants from water [197,198]. Most of the reported studies use bare or doped TiO₂ and ZnO, with different arrays [199–201]. On the other hand, metal-organic cages are combined with semiconductors, resulting in visible-light active micro-photoreactors for green H₂ production [202]. More recently, Claes et al. [195] reported the synthesis of translucent packed-bed TiO₂ based micro-photoreactors achieving an outstanding performance to degrade methylene blue as well as energy efficiency and displaying a photocatalytic space-

time yield (PSTY) of $0.657 \text{ m}^3 \text{ day}^{-1} \text{ m}^3 \text{ reactor KW}^{-1}$ under visible-light irradiation; such results are higher than that reported in previous works [196]. To achieve the upscaling of the micro-photoreactors, high-throughput methods must be used to accurately synthesize thousands of reactors in parallel for treating high volumes of water.

The miniaturization of the synthesis process in high-throughput methods promotes the compliance of GCP 1, by reducing the reagent consumption and the generation of wastes. Additionally, combinatorial methods look for increasing the atom economy (GCP 2) by optimizing the proportions of the reagents to achieve the finest composition that results in the highest photocatalytic performance. One example of this is the synthesis of $\text{g-C}_3\text{N}_4$, with a bandgap energy of $\approx 2.7 \text{ eV}$, which can be reduced by promoting the occurrence of nitrogen vacancies [203]. The synthesis of N-defective $\text{g-C}_3\text{N}_4$ is normally achieved using NH_3 in excess [204]. Through combinatorial methods, the optimal composition of $\text{g-C}_3\text{N}_4$ is obtained in a miniaturized scheme, reducing the production of hazardous residues, thus achieving the atom economy to obtain the most efficient photocatalytic material that can be directly used in scaled systems.

Regarding the Green Engineering Principles, using combinational methods for the synthesis of new or improved photocatalysts prevents contamination over treatment (GEP 2) and maximizes the use of reagents and energy (GEP 4), while a minimal quantity of materials is synthesized to meet the needs of the tests prior to upscaling, thus avoiding the production of excess (GEPs 5 and 8). Lastly, using micro-photoreactors for the degradation of pollutants in water streams observes the complying of GEPs 3 and 4, as the operation is designed to minimize the use of materials and energy in a purification process.

5.2. The Application of Virtual High-Throughput Methods to Migrate from the Edisonian to the Theoretical Approach

Combinatorial synthesis and characterizations are used in tandem with computational screening studies to discover new photocatalysts or allow for more in-depth investigation of existing materials to find better performances [205]. By this approach, researchers evaluate several key parameters of a library of materials using computational tools to find the best candidates to perform the photocatalytic process. So far, DFT-based high-throughput calculations are the most commonly used to propose new photocatalysts based on their physical, chemical, and optoelectrical properties [206]. The application of large-scale computational screening methods to develop nanometric materials is possible by exploiting the capabilities of supercomputers and using the existing databases of photocatalysts, therefore this kind of studies has increased in the last decade [207]. Most of the high-throughput computational screening studies are aimed at the discovery of new photocatalysts for the water splitting process [208–211]. For example, Zhang et al. [208] selected 205 layered materials over 50,000 inorganic compounds from the Materials Project Database as precursors to obtain 2D monolayers for green H_2 production. By considering the bandgap value and the potential of the conduction band (0 eV vs. NHE at $\text{pH} = 0$), the authors reported 36 semiconductors that satisfied the conditions for photocatalytic water splitting. The list included calcogenides, arsenides, and halides (e.g., GeAs_2 , GeTe , TiPbO , and Mo_2SBr_2). Moreover, 44 type-II heterojunctions were proposed based on the following criterion: (a) the valence and conduction band position, (b) the activity for water splitting at a range of pH values, and (c) the lattice parameters of the two semiconductors. Some examples of the selected heterostructures are $\text{MoS}_2/\text{MoSe}_2$, WS_2/WSe_2 , and MoS_2/WS_2 . More recently, Liu et al. [212] developed a first-principles high-throughput screening across more than 1000 potential bulk piezo-photocatalytic materials for green hydrogen production, proposing a set of 16 highly promising piezo-photocatalysts based on their optoelectronic properties and band alignment tunability; this group included BiTeCl , GaN , MgTe , and SeBr , among others.

Using high-throughput computational studies, the synthesis of new photocatalytic materials is dramatically reduced, which results in zero wastes (GCP 1) and the limited production of potentially hazardous materials (GCP 3). The development of methods that predict the ab initio properties of the materials allows to look for safer photocat-

alysts by using less-toxic solvents, increasing the energy efficiency and preventing the formation of undesirable by-products, thus addressing GCPs 4–6 and 11. By performing high-throughput computational screening studies, material researchers migrate from the Edisonian approach, characterized by the trial-and-error discovery, toward the systematic theoretical approach. The latter is in line with some of the Green Engineering Principles, by developing products (materials), procedures (synthesis and characterization), and systems (photocatalysis tests) output pulled rather than input pushed (GEP 5). This is because only the most effective—at least theoretically—photocatalysts are synthesized in the exact amount required to produce the maximum conversion, preventing wastes (GEPs 2 and 8) and maximizing mass, energy, and time consumption (GEP 4).

Machine learning, a subgroup of artificial intelligence, extracts the data of the synthesis and characteristics of photocatalytic materials from the high-throughput schemes to feed a set of algorithms and build models that ultimately make predictions on the performance of the photocatalysts. The stages for constructing machine learning models are: (a) data collection to form a training data set; (b) create and choose mathematical descriptors that encode the characteristics of the materials; (c) select a proper algorithm to build the model; and (d) to assess the quality and predictive capacity of the model [213]. Machine learning represents a paradigm shift in how new photocatalysts are designed, synthesized, and tested at the laboratory scale [214], which inherently covers several of the Green Principles. Machine learning finds its finest point when is coupled to automation, as it can be jointly used to upscale the synthesis of photocatalysts. For example, Tao et al. [215] integrated machine learning and microfluidics to accelerate the identification and optimization of the reaction conditions to obtain nanosized photocatalysts. The authors performed 160 experiments in a microfluidics platform, using different synthesis protocols to produce Au nanoparticles by green routes, while machine learning algorithms found the relationship between the synthesis conditions and the reactivity of the formed nanoparticles. There are so many challenges to face in the way ahead, but we consider that the next generation of photocatalyst will be produced, tested, and upscaled following the Green Principles and with a great support from computational chemistry.

6. Perspectives

Heterogeneous photocatalysis is a promising process in environmental remediation and energy generation and there are many unexplored possibilities in this area of research. Through the years, many attempts have been performed to upscale the photocatalytic water treatment; nevertheless, very few works have been published showing the settlement of the research in the production of new photocatalytic materials at higher scale. One reason is the inadequate funding for applied investigation in most countries; changing this paradigm is one of the most challenging tasks for the future and can be achieved through the continuous efforts of upscaling in universities and research centers that foster the interest of governments and funding associations to provide more resources in this matter. Sunlight harvesting using heterogeneous photocatalysis can be a reality in countries where sunlight irradiation is available throughout the year; therefore, some funding programs promoted by developed countries to implement technological advances in developing countries can aim at using upscaled photocatalytic systems in impoverished zones. Some upscaled systems have been successfully tested in developed countries such as Germany, Spain, and China. It is time that this kind of technology reaches densely populated dry zones where the necessity for safe water is high; this will enable science and technology to be applied to address social problems related to water scarcity and green fuel production.

Green Principles must be integrated into the heterogeneous photocatalysis process from a cradle-to-grave perspective, considering the pollution produced from the photocatalyst synthesis, its use through several reaction cycles, and its disposal when their lifetime is over. The GEPs should be especially considered when scaled systems are proposed and used either for water treatment or green H₂ production. Each year more and more publications include the term “green”; however, this term should be moderated and adjusted only

for materials that meet most of the Green Principles and Life Cycle Analysis. Following the GCPs and GEPs is the way ahead, which seems challenging. New problems arrive when these principles are applied since new variables are integrated. Indeed, more research and safety measures are necessary to upscale the water-splitting process. Future investigations should take this process from the laboratory in industrial plants; the potential revenues foreseen in the green fuel industry could promote new research in this unexplored field.

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