

Review

Synthesis and Application of Innovative and Environmentally Friendly Photocatalysts: A Review

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Abstract: Modern society faces two major challenges: removing pollutants from water and producing energy from renewable sources. To do this, science proposes innovative, low-cost, and environmentally friendly methods. The heterogeneous photocatalysis process fits perfectly in this scenario. In fact, with photocatalysis, it is possible both to mineralize contaminants that are not easily biodegradable and to produce hydrogen from the water splitting reaction or from the conversion of organic substances present in water. However, the main challenge in the field of heterogeneous photocatalysis is to produce low-cost and efficient photocatalysts active under visible light or sunlight. The objective of this review is to compare the new proposals for the synthesis of innovative photocatalysts that reflect the requirements of green chemistry, applied both in the removal of organic contaminants and in hydrogen production. From this comparison, we want to bring out the strengths and weaknesses of the proposals in the literature, but above all, new ideas to improve the efficiency of heterogeneous photocatalysis guaranteeing the principles of environmental and economic sustainability.

Keywords: innovative photocatalysts; green synthesis; codoped photocatalysts; pollutants degradation; hydrogen production



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1. Introduction

In recent years, the development of industrialization and the constant growth of the population have led to an increase in the need for effective processes for the removal of contaminants, in particular from water, which at the same time, can facilitate the enhancement of waste substances present in wastewater. However, it is becoming increasingly difficult to have clean water because many organic compounds are widespread in industrial effluents, such as dyes, aromatic hydrocarbons, pharmaceutical compounds, pesticides, and heavy metal ions [1]. The latest advances in sensing and monitoring technologies have made it possible to classify some pollutants as emerging contaminants (EC) that can be divided into persistent organic pollutants (POPs), pharmaceuticals and personal care products (PPCPs), and endocrine disrupting chemicals (EDCs), according to their use and origin, in order to facilitate their removal [2,3]. Conventional physical, chemical, and biological methods have been used for wastewater treatment. However, many organic compounds are resistant to such treatments, which are, therefore, limited by low removal efficiency, high operating costs, process complexity, and slow operation [4–6]. Nowadays, advanced oxidation processes (AOPs) appear as promising technologies for the degradation of nonbiodegradable pollutants [7]. AOPs are oxidation processes carried out under ambient conditions. AOPs are involved in the generation of highly reactive species, such as hydroxyl radicals ($\bullet\text{OH}$), in order to remove organic or even some inorganic compounds that cannot be oxidized by conventional oxidants (gaseous oxygen, ozone, and chlorine) until the assurance of their complete mineralization, in which CO_2 and H_2O are obtained [8,9]. Among different AOPs, heterogenous photocatalysis is a low-cost and environmentally benign technology widely used in water and in the air purification field. Heterogenous photocatalysis is based on the use of metal oxide semiconductors (TiO_2 , ZnO , WO_3 , Fe_2O_3 , ZnS , CdS , etc.) as catalysts and

an irradiation source [10–12]. The interest in heterogeneous photocatalysis started many decades ago, when in 1972 Fujishima and Honda developed the photochemical splitting of water into hydrogen and oxygen in the presence of TiO_2 [13]. In recent years, research has focused attention on the application of semiconductors as photocatalysts for the removal of organic and inorganic substances from aqueous or gaseous systems in environmental remediation, in the treatment of drinking water, and in plants' industrial and sanitary applications. The semiconductor metal oxide, especially TiO_2 , is able to convert light energy into chemical energy in order to decompose pollutants in air and water through oxidation and reduction processes [10].

Over the last few years, research has focused on the development of innovative heterogeneous photocatalysts through the design of sustainable and green synthetic approaches [14,15]. This need arose in order to try to satisfy the principles of green chemistry, including eliminating the use of toxic reagents and solvents dangerous to the environment [16]. These strategies range from the use of plant extracts to the valorization and recycling of metals in industrial waste, or from the use of solventless techniques to the elaboration of mild-reaction condition synthetic tools [17].

Currently, scientific literature is highlighting advances in the development of visible-light-active heterogeneous photocatalysts based on two different approaches: the design of sustainable synthetic methodologies and the use of biomass and waste as sources of chemicals incorporated into the final photoactive materials. The innovative spirit of the scientists guided the research on active photoactive materials with visible light for numerous applications. Particular attention should be paid to photocatalysts developed from environmentally friendly syntheses. This approach, in fact, follows the principles of sustainable development and fully fulfills the idea of green transition: there is no real benefit in the development of a material with high photocatalytic activity, but with a negative impact on the environment due to its unsustainable production. Many research groups have, therefore, developed several ecological and environmentally friendly photocatalysts.

The purpose of this review is to provide information about the latest developments in innovative photocatalysts, focusing on materials active in the presence of visible light, prepared through innovative doping methods (such as codoping) or prepared through the valorization of biomass and waste. In detail, this work describes, in separate sections, innovative photocatalysts (specifically TiO_2 -based photocatalysts) produced through sustainable processes (i.e., focusing on synthetic steps) used for water depollution, and innovative and noble metal-free photocatalysts, used for hydrogen production. In particular, the first part of this review concerns the application of active photocatalysts in visible light, then doped through different techniques and used for the removal of contaminants from water. In the second part, some alternative synthesis methods are reported, which involve the use of waste materials or avoid the use of harmful solvents used for the production of hydrogen. Finally, the conclusions report some considerations regarding the so-called "green" methods proposed for the synthesis of photocatalysts, which are also reported in this review.

2. Innovative Methods for Doping Photocatalysts: Codoped Photocatalysts

The photocatalytic process, in particular based on TiO_2 materials, is applied in different fields, including medical research, drug delivery, antibacterial products, energy storage, pollutant degradation, water splitting, dye-sensitive solar cells, and self-cleaning [18]. TiO_2 material is widely used as a photocatalyst for its low cost, good optical activity, high chemical stability, and nontoxic nature. TiO_2 is an n-type semiconductor, and it exists in three crystalline phases: anatase, rutile, and brookite. The anatase phase evidences the best photocatalytic activity of TiO_2 semiconductors because of its separation capacity of photogenerated holes and electrons between VB and CB under UV light [11]. Several factors affect the TiO_2 photocatalytic activity, such as pore volume, specific surface area, particle size, morphology, and bandgap energy.

The main drawbacks of bare TiO₂ are due to its large bandgap equal to 3.0 eV for the rutile crystalline phase and 3.2 eV for the anatase phase and the high-rate recombination of photogenerated electron-hole (e⁻/h⁺) pairs, which limits the photocatalytic efficiency. In order to activate the degradation process of water pollutants, TiO₂ is normally excited by UV light at a wavelength <387 nm. However, UV light represents only 5–8% of the solar spectrum at sea level. Therefore, the aim of researchers is to activate the catalysts by natural sunlight and prevent the photogenerated electron-hole pair recombination. A possible strategy to reduce the bandgap by extending the photo response of the catalyst to the visible light region is chemical modification through the doping of the crystal structure of TiO₂ with metals or with nonmetals. The addition of the dopant elements can inhibit the recombination of photo-induced holes and electrons by increasing the charge separation in order to achieve complete degradation in a very short time, also in the presence of a small amount of photocatalyst. The TiO₂ lattice can be modified by the introduction of transition metals, noble metals, and rare earth (RE) elements. Doping TiO₂ with transition metal ions (for example, Fe, Zn, V, Cr, Co, Mn, and Ni) and with Ag, Au, and Ru, generates a red shift in the absorption band of semiconductors from the UV to the visible region, resulting in an improvement in photocatalytic efficiency [19]. The inserted energy levels provide sub-bandgap irradiation from which electrons can be excited by lower energy photons than are required by undoped photocatalysts, and thus transferred from dopant d-band to CB or from VB to dopant d-band. In some cases, the presence of metal dopants enhances charge separation as well as interfacial charge transfer, while in many other cases, the metal dopants actually generate the rapid charge recombination, thereby reducing the electron diffusion length and lifetime [10,20,21]. In the literature, TiO₂ doping with Fe ions was widely investigated because the ionic radius of Fe³⁺ (0.64 Å) is smaller than that of Ti⁴⁺ (0.68 Å). Therefore, Fe ions can be easily incorporated into the TiO₂ lattice in order to increase charge transfer, and thus cause a reduction in the size of particles. This can lead to a high surface area, which could favor the stronger adsorption of contaminants on the surface photocatalyst [22,23]. Sood et al. described the application of Fe-doped TiO₂ photocatalyst in the field of environmental remediation for visible light-driven degradation of highly stable and toxic molecules, such as para-nitrophenol and methylene blue dye [24]. Likewise, the photocatalytic activity of Fe-doped TiO₂ and Ni-doped TiO₂ was tested for wastewater treatment to remove methylene blue from water under visible light [25,26]. Furthermore, researchers studied visible light-induced degradation of the acid orange 7 azo dye present in textile wastewater, the removal of the 2,4-Dichlorophenoxyacetic toxic herbicide and nitrobenzene from water and soil using Fe-doped TiO₂ photocatalysts [27,28], while Bi-doped TiO₂ and Ni-doped TiO₂ photocatalysts were used for the degradation of ibuprofen anti-inflammatory drugs under solar irradiation [29]. In addition to the application in the field of water and soil decontamination, TiO₂ doped with metals, for example, Co, evidenced high ferromagnetic properties, resulting in the adequate use of spintronic devices, such as spin transistors, nonvolatile storage, and spin logic devices [30]. Cu²⁺ (0.73 Å) is also a good dopant element for decreasing the bandgap due to its similar ionic radius [31] with respect to that of Ti⁴⁺ (0.68 Å). Many researchers confirmed the presence of Cu²⁺ ions in TiO₂ matrices in an interstitial way, which acts as electron acceptors or substitutes for one of the Ti⁴⁺. Krishnakumar et al. focused their study on photocatalytic mineralization of reactive red 198 using Cu-doped TiO₂ powders. The photocatalyst doping with Cu results in the generation of new energy states and the optical bandgap energy decreases, improving the photocatalytic degradation process [32]. The photocatalytic performances of TiO₂-based photocatalysts doped with noble metals have been considered in the field of air purification for the removal of toluene, which is one of the volatile organic compounds present in the urban atmosphere polluted by vehicle exhausts and by the use of solvents [33]. On the other hand, various literature studies have demonstrated that the TiO₂ doping process with rare-earth (RE) elements prevents the photogenerated electron-hole pair recombination, confirming a better visible light degradation of organic compounds present in water and in air [34–36]. The visible light activity of Pr-doped TiO₂ powders

in the degradation of rhodamine B and crystal violet [37] and also in the mineralization of phenol [38] was investigated. Among different EDCs, bisphenol A was treated in the presence of visible light using a Pr-doped TiO₂ photocatalyst [39]. Sm-, Er-, Gd-, and Ce-doped TiO₂ photocatalysts reported an interesting visible light-driven activity in the degradation of dyes and water-soluble phenolic compounds [40–42]. The photocatalytic activity of nonmetal-doped photocatalysts under visible light irradiation is commonly investigated for the removal of several dyes [43,44]. However, the dyes tend to absorb visible light, and consequently, the photocatalytic reaction could be induced not only by the absorption of visible light from the photocatalyst, but also from the photo absorption of radiation by the dye (i.e., sensitization of the dye) [45–49].

Among all the nonmetal dopants, nitrogen is the most commonly used due to its small ionization energy and its atomic size compared to that of oxygen [45]. The introduction of nitrogen as an impurity in TiO₂ is an efficient way of improving the solar light harvesting ability and photocatalytic activity of N-doped TiO₂ compared to bare TiO₂. N-doped TiO₂ photocatalysts can be used for a wide range of applications, such as the degradation of organic pollutants (i.e., dyes and drugs) [50,51] and air purification, sensors, solar energy conversion, and photovoltaics owing to their nontoxicity, ease of synthesis, low cost, and high chemical stability [52–54]. In addition to the degradation of industrial textile effluents, N-doped TiO₂ is utilized as a self-cleaning material for air purification and teeth whitening [55,56]. The effect of N and its amount in the TiO₂ structure on photocatalytic performance is widely described in the literature [57,58]. It is indeed reported that the incorporation of N in the TiO₂ structure induces the generation of an N 2p band above the original O 2p valance band, leading to the bandgap reduction with an increase in the photocatalytic activity under visible light [59]. In particular, the oxygen sites of TiO₂ can be partially replaced with nitrogen ions with the formation of oxygen vacancies and an increase in Ti amount as the content of N increases. Both oxygen vacancies and Ti species act as hole traps, inhibiting the recombination of electron-hole pairs and, therefore, improving the photocatalytic activity under visible light [60]. However, an optimal amount of dopant elements is required to ensure an improvement in photocatalytic performance because the presence of an excessive number of dopant ions in TiO₂ could favor the recombination phenomena of the electron-hole pairs, causing a worsening of the photocatalytic activity [61]. Bakre et al. demonstrated the effectiveness of N-doped TiO₂ catalysts in the degradation of cationic dye, methylene blue, and rhodamine B, under sunlight in comparison to commercial TiO₂ [62].

Other nonmetals, such as C, S, and P that use less than N, have been considered by several researchers to improve the optical response of TiO₂ in the visible light spectrum.

C-doped TiO₂ photocatalysts were also employed for the removal of organic compounds, such as dyes, pharmaceuticals, personal care products, and even bacteria from water [63], as well as for hydrogen production [64] and photoreduction of CO₂ [65]. Nonetheless, a majority of the literature is still focused on dye discoloration, while degradation and mineralization of other contaminants are less extensively investigated. It was observed that TiO₂ doping with C can occur by substitution of O ions with C ions, leading to a replacement of Ti-O by Ti-C bonds, by the replacement of Ti with C due to the rupture of Ti-O and creation of C-O bonds, or by the stabilization of C at the interstitial sites.

The application of S on TiO₂-based materials to provide positive effects for the photocatalytic activity is also discussed in the literature [66–69]. In general, the doping of TiO₂ with S element can be via cationic or anionic S routes. It was reported that cationic doping takes place by the substitution of titanium ions with S⁴⁺ or S⁶⁺, while anionic doping occurs with oxygen ion substitution with S²⁻.

Additionally, being that the ionic radius of S²⁻ (1.7 Å) is higher than that of O²⁻ (1.22 Å), the incorporation of sulfur by substitution of Ti⁴⁺ with S⁶⁺ is energetically more favorable than the replacement of O²⁻ with S²⁻ [70]. Both cationic and anionic S-doped photocatalysts revealed enhanced visible light photocatalytic activity. However, S⁶⁺ was found to be responsible for reducing the TiO₂ crystallite size and the cationic S-doped

TiO₂; the photoinduced holes and hydroxyls played a major role during photocatalysis. On the other hand, the S²⁻ doping resulted in an increased TiO₂ crystallite size, and in anionic S-doped TiO₂, the photoinduced holes and electrons played approximately the same role in the photocatalytic activity. In the case of the cationic and anionic S-doped TiO₂, the enhancement of the photoactivity was justified by the formation of Ti-O-S and O-Ti-S bands in the crystal lattice under the cationic and anionic S-doping, respectively, which introduced new impurity levels between the VB and CB. The photocatalytic activity of S-doped TiO₂ under visible light is usually investigated for the mineralization of different organic pollutants. In fact, Sharotri et al. examined the photocatalytic response of S-doped TiO₂ for various model compounds, such as rhodamine 6G (synthetic dye), quinalphos (an organophosphate pesticide), and diclofenac (a pharmaceutical waste), confirming the improved performance of doped nanoparticles with respect to bare TiO₂ [71]. Boningari et al. investigated the photodegradation of acetaldehyde with a cationic S-doped TiO₂ in the presence of visible light and revealed a higher efficient total organic carbon (TOC) removal of approximately 60% [72]. Bakar et al. examined the decomposition of methylene orange and phenol using both anionic and cationic S-doped TiO₂ in the presence of visible light and found that the efficiency of phenol photodegradation was similar to that observed for methylene orange [73]. The photodegradation of atrazine was also investigated. The studies revealed higher effectiveness of atrazine oxidation by the solar/S-doped TiO₂ system in comparison with the solar/TiO₂ system. The authors also emphasized that lower water pH favored the photodegradation of herbicide, while the presence of humic acids (HA) decreased the decomposition rate due to competition with the atrazine molecules for hydroxyl radicals and partial absorption of sunlight before it reached TiO₂ [74]. Lin et al. examined the synthesized S-doped TiO₂ in terms of the degradation of gaseous 1,2-dichloroethane [75]. S-doped TiO₂ photocatalysts exhibited superior photocatalytic activity under visible light compared to that of pure TiO₂. The conversion rate of 1,2-dichloroethane was 55.3 nmol min⁻¹ g⁻¹, whereas in the case of undoped TiO₂ it was 2.16 nmol /min·g after 60 min of irradiation. The S-doped TiO₂ synthesized by Baeissa et al. was applied for photo-oxidation of cyanide in water, reaching an efficiency of photocatalytic oxidation of cyanide equal to 100% after 30 min of irradiation with a blue fluorescent lamp [76]. Furthermore, the S-doped TiO₂ showed potential for application in the antimicrobial field. Dunnill et al. investigated the inhibition of E. coli growth in the presence of the S-doped TiO₂ films, recording the complete inhibition efficiency of bacterial growth after 24 h of irradiation. Recently, Zhang et al. studied the activity of P-doped TiO₂ photocatalysts for oxidative coupling of benzylamines and photodegradation of phenol under visible light irradiation. The enhanced performance of photocatalyst was attributed to the TiO₂ doping with P element, which can exist as a pentavalent oxidation state and can replace Ti⁴⁺ ions in the crystal lattice of anatase, by trapping photogenerated electrons in order to greatly reduce the recombination rate of electron/hole pairs [43].

In the last decade, for the treatment of wastewater containing biorecalcitrant organic pollutants, research interest has focused on TiO₂ codoping with two different ions, allowing better separation of photogenerated electrons and holes, and thus ensuring an effective enhancement of visible light adsorption together with the increased photocatalytic activity of TiO₂ [77].

The codoping process of a TiO₂ semiconductor can take place with metal/metal, metal/nonmetal and nonmetal/nonmetal. Thambiliyagodage et al. studied the effect of TiO₂ codoping with two transition metals, Fe and Cu, in the visible light-driven degradation of methylene blue. Fe³⁺ is introduced into the TiO₂ lattice via substitution because the cationic radii of Fe³⁺ and Ti⁴⁺ are quite similar. While, as Cu²⁺ (0.870 Å) ions are much larger than Ti⁴⁺ the introduction of Cu²⁺ into TiO₂ ions may occur in interstitial sites of the lattice.

Cu²⁺ belongs to the same group in the periodic table as noble metals, gold and silver, and therefore, it has similar properties due to its electronic configuration and the face-centered cubic structure. Furthermore, the authors observed that Cu can exist as copper

oxides, Cu_2O and CuO , generating heterojunctions with TiO_2 that lead to an improvement of the charge carrier separation with an increase in their lifetime, and enhancement of the interfacial charge transfer efficiency, resulting in higher activity of the photocatalyst under visible light [78–80]. Mancuso et al. investigated the photocatalytic performance of Fe-Pr-codoped TiO_2 photocatalysts in terms of color removal and mineralization efficiency for the treatment of aqueous solutions containing acid orange 7 dye under visible light irradiation by noting that the main reactive oxygen species which induce the contaminant photodegradation mechanism are superoxides and positive holes. It revealed the improvement in the photocatalytic activity, which should be related to the simultaneous doping of TiO_2 with Pr^{3+} and Fe^{3+} ions that produce a narrow bandgap together with an enhanced generation of oxygen vacancies, which can trap electrons, and therefore, reduce their recombination with photogenerated positive holes. The Fe-Pr-codoped TiO_2 material was also used for visible light degradation of phenol, confirming the absence of possible sensitization phenomena of the photocatalyst surface by acid orange 7 dye [81]. In order to develop efficient photocatalysts working with sunlight, some researchers tested the incorporation of transition metals Fe and Cr into the TiO_2 lattice by the codoping process. The photocatalytic systems exhibited two times higher for visible light decomposition of gaseous isopropyl alcohol (IPA) than single metal-doped TiO_2 nanoparticles due to the better optical properties in the range of 400–600 nm [82]. Liu et al. synthesized Zn-Mg codoped TiO_2 nanoparticles to evaluate the performance of the dye-sensitized solar cell, resulting in an improved conversion efficiency with respect to the solar cell based on undoped TiO_2 nanoparticles due to the faster carrier transport [83]. Additionally, in this case, the codoping of TiO_2 with metal and nonmetal substantially enhances the photodegradation activity of organic compounds with respect to undoped TiO_2 and single-doped TiO_2 , thanks to the further improvement of optical absorption towards the visible region. Qin et al. investigated the removal of pyrene, which is a polycyclic aromatic hydrocarbon used as a model pollutant, through a coupled photocatalytic-bacterial degradation process in presence of the Cu-N codoped TiO_2 , showing a better degradation efficiency under visible irradiation than UV light [84]. Visible light-induced degradation of organophosphate pesticides quinalphos and 2-chlorophenol using Mn-N-codoped TiO_2 photocatalyst and color removal of acid orange 7 with Fe-N-codoped TiO_2 powders with visible light were evaluated [85]. The use of C-N-codoped TiO_2 photocatalysts described allows for the shifting of light absorption from the UV region to the visible light region, assuring the increase in photocatalytic activity in terms of photodegradation of rhodamine B [86]. The potential application of the N-F-codoped TiO_2 powders to air purification was also investigated by simulating a commercial LED air cleaner system. The photocatalytic activity of N-F-codoped TiO_2 nanoparticles on the decomposition of acetaldehyde was superior to that of commercial TiO_2 . This outcome is due to the substitution of oxygen atoms both with N and P, which generates an increase in oxygen vacancies in the lattice, acting as a site for the formation of the active radicals involved in the degradation reaction [87]. P-N- TiO_2 photocatalysts were prepared for water splitting, which is a solar conversion process of energy into chemical energy (hydrogen and oxygen) for energy saving. In particular, as is largely discussed in the literature, the TiO_2 doping with N improves the optical absorption towards the visible region, ensuring a good photocatalytic performance. However, doping with N can induce the lattice long-range distortion in the TiO_2 crystal structure due to the substitution of O ions with N ions with the formation of oxygen vacancies, which, if present in excessive quantities, could act as recombination centers for holes and electrons, causing a worsening of the catalytic activity in the water splitting process. On the other hand, the presence of P together with N in the lattice reduces the long-range structural defects induced by N-doped TiO_2 and recovers the long-range ordered structure of TiO_2 crystals with a significant improvement in the separation of photoexcited electrons and holes by realizing the overall water splitting under visible light irradiation [88]. Below is a summary table with the main doped and codoped photocatalysts mentioned in this paragraph. Below, in the Table 1,

a summary of the described photocatalyst doped with different element, with the light source, is reported.

Table 1. Doped and codoped TiO₂ based catalyst.

Catalyst	Doping or Codoping Element	Light Source	Application
Fe-TiO ₂	Fe	visible	Para-niro phenol and methylene blue degradation
Ni-TiO ₂	Ni	solar	Ibuprofen degradation
Bi-TiO ₂	Bi	solar	Ibuprofen degradation
Cu-TiO ₂	Cu	visible	Red 198 dye removal
Pr-TiO ₂	(RE Element): Pr	visible	RhB and Crystal violet dyes removal
N-TiO ₂	Non metal: N	solar	Dyes removal
S-TiO ₂	Non metal: S	visible	Methyl orange and phenol removal
Fe-Cu-TiO ₂	Fe and Cu	visible	Methylene blue removal
Fe-Pr-TiO ₂	Fe and Pr	visible	AO7 dye removal
Cu-N-TiO ₂	Fe and Cu	visible	Pyrene removal

3. Main Synthesis Methods of Doped and Codoped Catalysts

The growing interest in the TiO₂-based photocatalysts led to the development of different preparation methods. Precipitation and coprecipitation, hydrothermal synthesis and sol-gel processes for the preparation of nanostructured materials are “wet” chemical methods, as they allow us to obtain solids with a high specific surface area and high porosity. Sol-gel is one of the most used methods for the preparation of visible active photocatalysts [89]. Solid particles homogeneously dispersed in a liquid medium in colloidal form and generate a sol, whereas an organized three-dimensional continuous solid arrangement having submicrometer size pores and containing the liquid phase produces a gel. Hydrolysis and polymerization reactions of different precursors (usually metal alkoxides) produce sol during a sol-gel preparation. The complete polymerization and the loss of solvent can induce the transition from the sol to the gel phase. Therefore, in a general way, the sol-gel method involves four basic steps: hydrolysis, polycondensation, drying, and calcination for precursor decomposition. In the case of UV activated photocatalysts doping, to induce activity by visible light irradiation, a solution containing the precursor salt of the doping element (metal or nonmetal) is inserted in the sol formation step. In fact, in this way, strong covalent bonds between the dopant element and the very reactive monomeric species of the semiconductor precursor (e.g., TiO₂ or ZnO) are created. Several photocatalysts active under visible light were prepared by sol-gel process, including TiO₂ doped with nitrogen, [90] boron [91], phosphorous [92], iron [22], cobalt [93], magnesium [94], nickel [95], cerium [96], zinc [97], barium [98] molybdenum [99], neodymium [100], and praseodymium [38]. The steps of the sol-gel method can be varied in order to enhance the doping efficiency. For example, visible active N-doped TiO₂ has been synthesized through a modified sol-gel process [101], in which the reactants were titanium isopropoxide (as TiO₂ precursor) and ammonia aqueous solution (as nitrogen precursor). The N-doped TiO₂ catalyst was obtained by a hydrolysis reaction between the two precursors. The preparation was carried out at 0 °C, under stirring, until the formation of a gel. This gel was centrifuged and washed with distilled water and then thermally treated in a furnace at 450 °C for 30 min. The characterization of the N-doped TiO₂ catalyst, yellow in color, evidenced the ability to absorb visible light, as indicated by the bandgap value (2.5 eV) [102] Similarly, the synthesis of Cr-doped TiO₂ nanoparticles was performed by a modified sol-gel method using a water-alcohol mixture as a solvent. A solution containing ethanol and isopropyl alcohol were mixed slowly with titanium (IV) butoxide under sonication at 40 °C in the ultrasonic bath for 30 min for good dispersion. To this solution, alcoholic gum powder was added drop by drop with constant magnetic stirring. The resultant precursor solution was mixed with distilled water containing chromium nitrate nonahydrate under constant stirring at 80 °C for 4 h. The excess solvent was removed by evaporation with continuous stirring; the resultant precursor was dried at 110 °C for 12 h and then finally calcined

at 500 °C for 4 h in a high temperature muffle furnace under static air atmosphere [103]. The sol-gel synthesis was also adopted for the preparation of codoped photocatalysts. For example, Fe-N-codoped TiO₂ was prepared using distilled water containing urea and mixed with a solution of titanium tetraisopropoxide and iron(II) acetylacetonate [77]. In the same way, to obtain Fe-Pr-codoped TiO₂ distilled water containing praseodymium nitrate was mixed with a solution of titanium tetraisopropoxide and iron acetylacetonate [81]. The systems were maintained at room temperature under continuous stirring for 10 min. Both suspensions were centrifuged for the separation of precipitates, which were washed with distilled water three times and finally placed in a furnace at 450 °C for 30 min in static air. The hydrothermal method requires both high temperature and water pressure values as operating conditions. When a solvent, different from water is employed, the method is called “solvothetical” [104]. The preparation of photocatalysts by the hydrothermal method is typically carried out in a steel vessel operating at high pressure (autoclave) under controlled temperatures; the formation of nanocatalyst occurs in the liquid medium.

When the reaction mixture is heated, two zones at different temperatures are formed inside the autoclave. In the higher temperature, upper zone, the reactants of the mixture form a solution, while the saturated solution present in the lower part of the autoclave moves to the upper section of the reactor because of the convective motion. When the solution in the upper part of the autoclave becomes cooler and denser, it moves down. Simultaneously, due to the temperature decrease, the solubility limit is exceeded and consequently, crystallization can start. This technique allows us to directly obtain the catalyst in powder form, while the crystalline degree can be tuned, depending on the operating conditions. In addition, particle size, shape, and chemical composition can be controlled by changing only two parameters, namely, the temperature of the reaction mixture and the solvent used in the synthesis, in order to reach high pressure values and consequently, supersaturation at lower temperatures. A literature study reported a comparison between the sol-gel and the hydrothermal synthesis to prepare TiO₂ photocatalyst for propene oxidation [105]. In both cases, a mixture prepared with titanium tetraisopropoxide and ethanol was stirred at room temperature, first magnetically for 1 h and then in ultrasonic bath (30 min). Then, a solution containing HCl and ethanol was added dropwise, and the mixture was left under continuous stirring for 1 h. The synthesis was also performed without HCl, and H₂O was added instead. In the case of the sol-gel method, the product of the above-described procedure was dried at 100 °C for 12 h. In the case of the hydrothermal synthesis, the product was transferred to an autoclave and maintained at 180 °C for 12 h and, afterwards, it was dried at 100 °C for 12 h. Finally, both the sol-gel and the hydrothermal samples were heated in air in a muffle at 5 °C/min moved up to 350 °C and kept for 2 h at this temperature. It has been found that TiO₂ materials with high crystallinity, between 67% and 81%, and surface area (up to 134 m²/g) were obtained with both sol-gel and hydrothermal methods. In general, the surface and pore volume of TiO₂ samples obtained by the hydrothermal method are larger than those of TiO₂ by sol-gel. TiO₂ catalysts for hydrothermal synthesis are, in general, more active than sol-gel materials or commercial TiO₂ (P25) in the photo-oxidation of propene. The effects, due to the presence of HCl during the synthesis of TiO₂ and of the post synthesis heat treatment are much more marked in the case of materials prepared via the sol-gel method. In particular, the hydrothermal method leads, in general, to higher crystallinity and allows us to obtain a larger amount of anatase using a low HCl concentration. In the sol-gel method, the presence of acid is necessary to enhance the crystallization and to obtain samples with acceptable surface area. Both sol-gel and hydrothermal methods are appropriate for obtaining photocatalysts with large surface areas (larger than that of P25) and, in general, TiO₂ samples obtained by the hydrothermal method have larger surface areas and pore volumes than TiO₂ by sol-gel technique. The post synthesis heat treatment of the sol-gel samples is necessary to develop crystallinity, particularly when no HCl is used in the preparation, whereas, the hydrothermal method leads to high crystallinity even without the use of HCl in the synthesis and without the post synthesis heat treatment [105]. Furthermore, the hydrother-

mal method is a very effective way of introducing dopant elements into the crystalline structure of TiO₂ or ZnO in the photocatalysts synthesis [106]. In particular, many papers have been devoted to the controlled synthesis of TiO₂ hollow particles, due to their high photocatalytic activity. For example, Zhou et al. prepared flower-like F-doped TiO₂ hollow microspheres with the hydrothermal synthesis method, controlling the hydrolysis of TiF₄ in a Teflon autoclave at a reaction temperature of 180 °C [107]. A visible active N-doped TiO₂ photocatalyst was prepared using triethylamine as a nitrogen source by a low-temperature hydrothermal method without any thermal treatment [108]. Fe-doped TiO₂ nanoparticles were directly prepared with TiO₂ nanoparticles and iron(III) nitrate nonahydrate was added into a Teflon-lined autoclave to hydrothermally react at 200 °C for 24 h [109]. It was found that the hydrothermal synthesis allowed the incorporation of Fe³⁺ into the inner matrix of TiO₂ and not on its surface in order to obtain the photocatalytic powders active under visible light with an improvement of degradation activity of the pollutant. Fe-doped TiO₂ anatase powders produced by a hydrothermal process with titanium(IV) tetra-*tert*-butoxide and FeCl₃ or FeCl₂ dissolved in *n*-octanol [110] evidenced small crystal sizes (11.4 nm) and high specific surface (101.4 m²/g) with respect to undoped TiO₂ (78 nm and 29 m²/g, respectively), while Fe-doped TiO₂ prepared by the sol-gel method using titanium tetraisopropoxide, ferric nitrate, glacial acetic acid, and absolute ethanol have high specific surface areas and exhibited smaller average crystallite sizes (4–8 nm) than undoped TiO₂ (11 nm), demonstrating that Fe³⁺ doping contains the grain growth of the TiO₂ photocatalyst. The hydrothermal method was also used to prepare photocatalysts different from TiO₂ and ZnO, which formed very high crystallinity structures. For example, Amano et al. [111] obtained a bismuth tungstate (Bi₂WO₆) catalyst possessing high photocatalytic activity under visible light irradiation. The hydrothermal method was also applied to prepare codoped TiO₂ photocatalysts. Ce-N-codoped TiO₂ was obtained with two solutions: solution A contained urea used as a nitrogen precursor and cerium nitrate hexahydrate as a cerium precursor with the addition of titanium(IV) butoxide and, solution B, which consisted of nitric acid and titanium(IV) butoxide. Solution B was added slowly into solution A at the rate of 1 mL/min under moderate stirring for approximately 2 h. The mixture was then transferred into a 100 mL of Teflon-lined autoclave, which was kept in an oven at 120 °C for 16 h. After the autoclave was cooled to room temperature, the precipitates at the bottom of the autoclave were washed with deionized water several times to remove the impurities. The obtained samples were kept in the oven at 100 °C overnight for drying. In order to have better crystallization and to remove the solvent and other impurities, the samples were calcined at 450 °C for 3 h [112]. It was observed that the codoped samples showed a remarkable increase in the visible light-induced degradation of acid orange 7, which can be associated with the smaller crystal size (8 nm for codoped sample), larger surface area (150 m²/g for codoped sample) than N-TiO₂ (16 nm and 67 m²/g), and pure TiO₂ (18 nm and 57 m²/g) and also related to the slow recombination rate of photoexcited electrons and holes. The same Ce-N-codoped TiO₂ sample was also synthesized by the sol-gel method [113]. Ceric ammonium nitrate and urea were dissolved in an aqueous solution with the addition of cetyltrimethyl ammonium bromide adjusting the acidity (pH 1) using phosphoric acid. Afterward, titanium(IV) butoxide was added dropwise to the acidified solution. When the titanium(IV) butoxide was completely hydrolyzed, the mixture was refluxed at 348 K for 24 h and, subsequently, dried under vacuum at 333 K for 4 h. The photocatalytic activity of the Ce-N-codoped TiO₂ nanoparticles was determined by measuring the removal of methylene blue under solar light irradiation, and its photodegradation efficiency (85%) was higher than the activity of N-doped TiO₂ (71%) and Ce-doped TiO₂ (58%). All the photocatalysts showed the anatase phase, but the codoped sample reported a smaller crystallite size (9.8 nm) even than the Ce-N-codoped TiO₂ obtained by hydrothermal treatment. Moreover, the codoped sample had a structure with wormlike channels and a mesoporous structure. The photocatalysts preparation through the precipitation method [114] involves the chemical transformation of a highly soluble metal precursor into another substance of lower solubility, which precipitates in solution. The conversion to the

low solubility compound (and then to the precipitate) is usually obtained by increasing the pH of the solution. In practice, the metal precursor is dissolved in a solvent (generally water). The obtained solution is thoroughly stirred and, after a given time, a precipitating agent is gradually, in a controlled amount, added. The formed solid precipitate is collected, washed, dried, and finally activated through thermal treatment. As declared above, raising the pH is the most common way to perform deposition-precipitation. To avoid a rapid precipitation in a solution that could lead to a remarkable increase in particle size, the mixing and precipitation steps should be carried out separately. At the laboratory scale, this is possible using a base, and this kind of precipitation method has been applied for the preparation of various catalysts. Upon raising the solution's pH, the precipitation of a hydroxide is expected. Fe-doped TiO₂ photocatalyst was synthesized by simple a deposition-precipitation route for the photodegradation of thiacloprid in the presence of H₂O₂ as an oxidant and UV light irradiation [115]. Fe-doped TiO₂ particles showed good sedimentation properties and stability toward photocorrosion, which indicates the possibility of the industrial applications of this photocatalyst for wastewater treatment. TiO₂ and Fe-doped TiO₂ particles for the photodegradation of gaseous toluene as a typical pollutant in air were prepared with the direct precipitation method with an impinging stream-rotating packed bed (IS-RPB) [116] as a reactor. TiO₂ and Fe-doped TiO₂ catalysts show narrow pore size distributions and a similar total pore volume (0.45–0.48 cm³/g) and average pore diameter (9.6 nm) with high specific surface area (123.5–148.5 m²/g), in comparison with commercial TiO₂ (P25) that presents a wide pore size distributions and a pore diameter of 30.6 nm with specific surface area of approximately 106 m²/g. Similarly, also for the catalysts formulated with the precipitation technique, the beneficial effect of the doping of iron in TiO₂ was observed, confirming the improvement of the photocatalytic activity under UV light with degradation efficiency of toluene equal to approximately 96% compared to 55% and 56% values obtained with pure TiO₂ and P25, respectively [117]. Moreover, the authors reported the preparation of Fe-Co codoped TiO₂ photocatalyst using the impinging stream-rotating packed bed and precipitation method mentioned above, in order to evaluate the decomposition of phenol both under UV and visible light [118]. The codoping of TiO₂ with Fe and Co ions increased the specific surface area (194 m²/g). The doping of TiO₂ with Fe ions can inhibit crystal growth, and thus increase the specific surface area. However, the specific surface area of the catalyst first increases (194 m²/g) and then decreases (88 m²/g); the total pore volume rises from 0.56 to 0.77 cm³ g⁻¹ as the Co²⁺ content increases in comparison with pure TiO₂ that exhibits a specific surface area of 148.5 m²/g and total pore volume of 0.45 cm³ g⁻¹. This result can be related to the introduction of an appropriate amount of Co²⁺ that can cause defects on the crystal surface, and Co²⁺ and Fe³⁺ act synergistically to increase the specific surface area of the catalyst. However, excess Co²⁺ can form new phases that may be deposited on the TiO₂ surface and block the pores, resulting in a decrease in specific surface area. The enhanced crystalline and optical properties of codoped TiO₂ demonstrated that the presence of Fe and Co ions into crystal lattice inhibits the recombination of photogenerated hole-electron pairs resulting in a better degradation activity. In fact, the decomposition efficiency of phenol after 2.5 h of UV and visible light irradiation was 88.71% and 24.58% for the Fe-Co codoped TiO₂ catalyst, which represents 1.59 and 2.07 times that of pure TiO₂ [118].

4. Recent Application of Innovative Photocatalysts

4.1. Photocatalytic Removal of Organic Dyes from Aqueous Solution

The dyes degradation cannot occur through biological techniques because the complex structure of dye molecules is resistant to microbial decomposition. Industrial activities involve a large consumption of dyes and their discharge into water bodies causes serious damage to the environment. A dye is a colored organic substance that absorbs visible light and can attach strongly to a fiber by means of chemical or physical bonding between the groups of fiber and dyes. Generally, dyes can be classified on the basis of their chemical structure as well as the existence of specific chromophores [119]. Dye is a highly toxic

organic substance, such as benzidine and aromatic amine, and many of them are very difficult to treat [120]. It causes eye and skin irritation, asthma, allergic contact dermatitis, and respiratory tract infections [121]. Azo dyes are readily converted into aromatic amines under potentially dangerous and environmentally toxic anaerobic treatment conditions. Dye hinders the photosynthetic activity of aquatic plants by delaying the penetration of light into the water, which makes oxygen unavailable for the biodegradation of microorganisms in the water [122].

On the contrary, the photocatalytic degradation process of dye is based on in situ generations of highly reactive hydroxyl radicals (OH•) that can rapidly and nonselectively oxidize any dye contaminant present in the wastewater.

Table 2 shows the visible light-driven performance of doped and codoped TiO₂ powders prepared by the above-mentioned synthesis techniques on the degradation of dyes (methylene blue, rhodamine B, and acid orange 7) used as model contaminants reported in the literature.

Table 2. List of doped and codoped catalysts used on visible light degradation of dye contaminant.

Catalyst	Preparation Method	Treatment Time (min)	Target Dye	Dye Concentration (ppm)	Degradation Efficiency (%)	Refs.
Fe-TiO ₂	sol gel	60	methylene blue	30	93	[123]
Mn-TiO ₂	hydrothermal	180	methylene blue	10	97	[124]
Mn-TiO ₂	hydrothermal	300	methylene blue	160	75	[125]
Ni-TiO ₂	hydrothermal	180	methylene blue	5	98	[126]
Ni-TiO ₂	hydrothermal	60	methylene blue	10	93	[26]
Sn-TiO ₂	sol gel	120	methylene blue	20	77	[127]
Al-TiO ₂	sol gel	180	rhodamine B	10	89	[128]
Al-TiO ₂	sol gel	60	Acid orange 7	5	99	[129]
Si-TiO ₂	sol gel	120	methylene blue	10	87	[130]
Pt-TiO ₂	Hydrothermal	90	rhodamine B	10	99.5	[131]
Pd-TiO ₂	sol gel	120	methylene blue	20	99.4	[132]
Fe-TiO ₂	sol gel	60	acid orange 7	10	73	[77].
Fe-TiO ₂	sol gel and mechanical alloying	240	methylene blue	2	78	[133]
Pr-TiO ₂	sol gel	60	acid orange 7	10	-	[81]
C-TiO ₂	sol gel	100	methylene blue	10	100	[134]
N-TiO ₂	sol gel	60	acid orange 7	10	55	[77]
I-TiO ₂	sol gel	240	rhodamine B	20	95	[135]
S-TiO ₂	hydrothermal	70	rhodamine B	10	95	[57]
C-N-TiO ₂	solvothermal	90	Rhodamine B	20	94	[86]
Fe-N-TiO ₂	sol gel	60	Acid orange 7	10	83	[77]
Fe-Pr-TiO ₂	sol gel	60	Acid orange 7	10	80	[81]
Fe-Ce-TiO ₂	sol gel	120	methylene blue	4	86	[136]
Fe-La-TiO ₂	sol gel	180	methylene blue	0.1	44	[65]
F-N-TiO ₂	hydrothermal	300	methylene blue	5	97	[137]

4.2. Photocatalytic Removal of Emerging Contaminants from Aqueous Solution

Emerging contaminants (ECs) are unregulated pollutants, for which legislative measures are required. They are not new chemicals, but they have persisted in the environment for some time [138]. They consist of the main components of different products used in daily life.

In particular, ECs include endocrine-disrupting chemicals (EDCs), pharmaceuticals and personal care products (PPCPs), persistent organic pollutants (POPs), and so on [139]. The development of techniques and methods of environmental analysis allowed the detection of these harmful substances in municipal wastewater [140], surface water [141], and drinking water [142].

Although the detected concentrations of these ECs in municipal waste, surface, and drinking water are very low, their chemical properties are relatively stable and susceptible to bioaccumulation. Therefore, they can cause severe damage to the ecological environment and human health [143,144]. For example, EDCs are highly dangerous for humans as they attack human organs, and some psychoactive substances could damage brain tissue in humans [145].

ECs are usually noxious residues caused by the frequent and improper consumption of products during human production and living activities [146]. These toxic residues are

excreted or discarded by humans and eventually enter wastewater treatment systems [147]. There are hardly any biodegradable drug residues discharged into surface waters together with wastewater from purification plants. Furthermore, these drug residues enter groundwater by runoff, diffusion, and infiltration of surface waters and, thus, can even pollute drinking water. There are also many ECs in the sludge from wastewater treatment systems. These sewage sludges are used for agriculture and cultural fertilization, and therefore, also surface waters are polluted.

In recent years, many studies have focused on photocatalytic technologies for EC removal [148].

For instance, Prieto-Rodriguez et al. reported that a low concentration of TiO₂ is suitable for the removal of EC in the effluents of wastewater treatment plants. Visible light-induced degradation of ECs using TiO₂-based photocatalysts doped and codoped with metals and/or nonmetals is largely described in the literature. Table 3 displays the activity of doped and codoped TiO₂ powders prepared by the above-mentioned synthesis techniques on the degradation of ECs under visible light [149].

Table 3. List of doped and codoped catalysts used on visible light degradation of ECs.

Catalyst	Preparation Method	Treatment Time (min)	Target EC	EC Concentration (ppm)	Degradation Efficiency (%)	Refs.
Ce-TiO ₂	sol gel	60	tetracycline	20	93	[150]
Bi-TiO ₂	sol gel	360	Ibuprofen	25	89	[29]
Ni-TiO ₂	sol gel	360	Ibuprofen	25	50	[29]
N-TiO ₂	sol gel	1200	mecoprop	580	50	[151]
Fe-TiO ₂	sol gel	75	Paraquat dichloride	30	98	[152]
Fe-TiO ₂	sol gel	200	Gesaprim Herbicide	40	90	[153]
Mn-TiO ₂	hydrothermal	300	glyphosate	6	75	[154]
N-TiO ₂	sol gel	330	lindane	100	100	[154]
Cr-TiO ₂	sol gel	330	lindane	100	30	[154]
Ag-TiO ₂	sol gel	330	lindane	100	23	[154]
Fe-TiO ₂	sol gel	330	lindane	100	10	[154]
Fe-Cr-TiO ₂	sol gel	330	lindane	100	37	[154]
N-S-TiO ₂	sol gel	90	aldicarb pesticide	19	>80%	[155]
Fe-N-TiO ₂	sol gel	240	amoxicillin	30	59	[156]
Fe-N-TiO ₂	sol gel	240	streptomycin	30	50	[156]
Cu-S-TiO ₂	sol gel	90	ciprofloxacin	15	100	[157]
Fe-N-P-TiO ₂	sol gel	180	thiachloprid	0.5	29	[158]
C-N-B-F-TiO ₂	sol gel	480	thiamethoxam	87.5	65	[159]
C-N-B-F-TiO ₂	sol gel	450	imidacloprid	24	71	[159]

4.3. Photocatalytic Degradation of Phenolic Compounds

Phenolic compounds consist of aromatic compounds whose hydrogen is substituted with hydroxyl groups (–OH) on aromatic rings. They can be substituted with chlorine atoms or nitrated or alkylated to produce a series of corresponding derivative compounds. The hydroxyl groups in phenolic compounds can form hydrogen bonds with water molecules. Phenolic compounds can be divided into endogenous and exogenous phenolic compounds [160]. Endogenous phenols exist in nature and are generally derived from roots, stems, leaves, fruits, and other parts of plants or crops. While exogenous phenols are usually produced by smoke from biomass combustion and vehicle exhaust. In the atmosphere, phenolic compounds with substituent groups, such as methoxy (–OCH₃), methyl (–CH₃), carbonyl (C=O), and carboxylic acid (–COOH) are ubiquitous aromatic compounds. In fact, the important emissions from biomass burning of catechol and guaiacol were observed [161].

Moreover, some phenolic compounds are also produced during the manufacturing and industrial processing of products. For example, they are obtained in the coking and refining process as main products extracted from oil and coal mines [162]. Another important source of phenolic compounds is organic chemical synthesis. Domestic and industrial activities, such as phenolic resin manufacturing, oil industry, pesticide synthesis, plastics,

coking operations, wood products, pulp, textiles, detergents, and pharmaceuticals, have discharged harmful and toxic phenolic compounds to water bodies, including rivers, lakes, and seas [163]. In particular, chlorophenols can be produced by the paper industry [164]. Methylphenols, chlorophenols and 2,4-dinitrophenol are widely used as synthetic intermediates for pesticides, preservatives, herbicides, and dyes [165]. Cyanophenols can be used as a precursor to synthetic drugs and antifungal agents [166]. Phenols are a class of organic weak acidic compounds with higher solubility in water, which are hard to degrade since they require a longer time to degrade and tend to accumulate in the environment. Therefore, the excessive use of phenols and their derivatives further increases the risk of environmental pollution. Some phenolic compounds, such as nitrophenols can influence the photochemistry of the atmosphere, the quality of the air and the earth's climate due to their strong absorption of UV light and visible light. In soil or water, phenolic pollutants can change their pH, having negative effects on animals, plants, and micro-organisms. Phenolic compounds are highly toxic organic pollutants that invade the human body through the mucosa, digestive tract, respiratory tract, and skin, chemically reacting with proteins in the body. In this way, the protein is denatured and coagulated, resulting in cellular inactivation. Chlorophenols and alkylphenols are typical environmental endocrine disruptors (EDCs), present in water and soil which can damage human organs due to their embryotoxic and teratogenic nature [167]. For this reason, to avoid threatening the water environment and air quality, phenolic pollutants need to be treated effectively. AOPs have been successfully applied to industrial wastewater treatment, leading to the generation of powerful reactive species, principally the hydroxyl radicals and sulfate radicals.

AOPs can destroy the structures of aromatic rings, reduce biological toxicity, and break long-chain molecules that result in high-efficiency treatment of organic pollutants. For example, H_2O_2 /UV-C and photo Fenton treatment can completely degrade 2,4-dichlorophenol with high TOC removal [168]. In the field of heterogeneous photocatalysis, high activity in phenol degradation under visible light irradiation was observed using TiO_2 materials made active by codoping with metals and nonmetals [169,170]. In this regard, many studies in the literature discuss the visible light driven-degradation of different phenolic compounds in aqueous solutions using doped and codoped TiO_2 materials. Table 4 shows the activity of doped and codoped TiO_2 powders prepared with the above-mentioned synthesis techniques on degradation of phenolic compounds under visible light.

Table 4. List of doped and codoped catalysts used on visible light degradation of phenolic compounds.

Catalyst	Preparation Method	Treatment Time (min)	Target Phenolic Compound	Phenolic Compound (ppm)	Degradation Efficiency (%)	Refs.
N-TiO ₂	hydrolysis precipitation	120	phenol	50	100	[171]
N-TiO ₂	hydrothermal	120	phenol	20	36	[172]
N-TiO ₂	hydrothermal	600	phenol	25	81	[170]
Ag-TiO ₂	sol gel impregnation	360	4-chlorophenol	10	73.5	[173]
Fe-TiO ₂	sol gel	210	phenol	10	30	[174]
N-TiO ₂	hydrothermal	600	4-chlorophenol	130	17	[99]
Sm-TiO ₂	hydrothermal	600	4-chlorophenol	130	1.5	[175]
Ce-TiO ₂	sol gel	240	2-chlorophenol	10	100	[176]
Fe-TiO ₂	sol-gel and mechanical alloying	240	phenol	5	40	[133]
Sm-N-TiO ₂	hydrothermal	600	4-chlorophenol	130	40	[175]
N-Zr-TiO ₂	sol-gel	1400	4-nitrophenol	14	68	[177]
Cr-V-TiO ₂	sol gel	180	phenol	5	50	[178]
Pt(II)-Cr-TiO ₂	sol gel	180	phenol	5	70	[178]
Fe-Pr-TiO ₂	sol gel	240	phenol	10	66	[81]

At this point, considering the results summarized in the previous tables, it is possible to make some reflections regarding the pros and cons of the synthesis methods typically proposed in the literature, and some consideration about the role of doping and codoping elements and their effect on the photocatalytic performance.

Regarding the synthesis methods, it is clear that it is mainly the “sol gel” method or the “hydrothermal method”. In particular, the recurrent choice of the sol-gel synthesis method is certainly explained by its intrinsic ease of execution. In fact, it is a method characterized by easily manageable operating conditions (P and T) [179]. Therefore, it is possible to define “sol gel” an ecological and simple method as it does not require complicated synthesis conditions or tools and it is known to be an inexpensive technique. Furthermore, it allows us to control the particle size and is quite flexible with the addition of other elements, which act as dopants for the semiconductor [180,181]. In fact the sol phase increases the covalent bond between the dopant species and the monomer species of the semiconductor [179]. On the other hand, there is the risk of the phenomenon of “shrinkage” and aging of the gel, which involves a failure of the synthesis process. In addition, long processing times may be required and sometimes, the presence of impurities may be found. Considering the hydrothermal synthesis, this method also presents pros and cons in the preparation of heterogeneous catalysts. In particular, in regard to the advantages, it can be highlighted that with this method most of the precursor material can be made soluble in a suitable solvent by heating and pressing the system near its critical point. Moreover, easy and precise control of the size, shape distribution, and crystallinity of the final product by adjusting parameters, such as reaction temperature, reaction time, type of solvent, type of surfactant, and type of precursor, can be obtained. Specifically, this method is effective in the realization of high quality 1D nanostructures, especially nanorods. Moreover, easy addition of additives for doping is possible with hydrothermal synthesis [182]. On the other hand, this method is configured as a “black box”. In fact, using the autoclave, it is not possible to observe the reaction and correct the operating parameters in real time. Furthermore, the required temperature and pressure values are typically high, and therefore, require suitable equipment (the autoclave).

As for the considerations of the elements for doping and codoping, it can be said that the modification of the TiO₂ semiconductor is essential to improve its performance in several respects. Surely an important fact concerns the possibility of using light sources other than UV (both for economic, ecological and safety reasons), therefore, for example, visible or solar light. This can only be possible through the doping of TiO₂. The literature proposes various solutions to achieve this goal. In fact, it is possible to exploit the potential of noble metals (such as Au, Pt, Ag, and Pd), which greatly improve the photocatalytic performance of TiO₂ both under UV irradiation and visible light. It should be emphasized that the use of noble metals is proposed above all to induce a modification of the surface of the semiconductor rather than its crystal lattice [183]. However, this solution does not produce a modification of the bandgap, therefore, of the absorption capacity of light sources other than UV, as it avoids the recombination of the electron-hole pair that typically affects semiconductors such as TiO₂, and which must be kept stable to ensure the performance of the photocatalyst [184]. When nonmetallic elements are used, they typically enter the crystal lattice of the semiconductor, replacing an atom whose atomic radius is more similar in size, and acting with the oxygen atoms, and thus causing a change in the electron densities of the oxygen [185–187]. This causes a change in the atomic energy level of the oxygen atom with a consequent modification of the catalyst bandgap [188]. This allows the semiconductor (TiO₂) to absorb light at a different wavelength.

The codoping approach allows for further improving the properties of the final material. In fact, with a codoping it is possible to act on the electronic, but also the chemical and magnetic properties of the starting semiconductor [189]. Literature studies show that titania codoping improved the ability of absorbing visible light compared to single element doped titania [181,190]. The role of codopants is not only in narrowing the bandgap, but also contributes to the formation of different heterostructures, such as the formation of different

electronic structures with TiO₂ [191]. Studies have shown that codoping of TiO₂ produces synergistic effects that can further enhance the photocatalytic properties of TiO₂ [188,192]. Furthermore, the choice of compatible codopants and the most suitable synthesis methods for the introduction of the dopant are crucial as they affect doping levels [181,191].

5. Innovative Photocatalysts for Hydrogen Production

Hydrogen is an attractive carrier of green energy due to its energy content and the lack of greenhouse gas emissions after its combustion. Currently, the main hydrogen production technologies involve fossil fuels: hydrogen is produced mainly through steam reforming and water gas shift processes [193]. Additional collateral technologies for its production include chemical, electrochemical, biological, and thermal processes. The possibility of producing energy using solar energy has attracted increasing interest in recent years. In particular, the thermochemical [194], photoelectrochemical [195] and photochemical [196] processes can be used for the generation of solar hydrogen. The photocatalytic generation of hydrogen can be obtained through the photolysis of water or the photoreformation of organic species [197]. The photocatalytic splitting of water consists of the decomposition of water into hydrogen and oxygen by reaction with photogenerated charge carriers. Photocatalytic reforming is based on the ability of organic species (i.e., sacrificial agents) to be oxidized by photogenerated positive holes and to release protons, which in turn generate hydrogen by reacting with photoelectrons. The scientific literature proposes several studies on this topic, and several catalytic formulations have been studied. At this point, when can we define a photocatalyst as “innovative?”

We certainly know when a catalyst can be considered “efficient.” As also reported by Clarizia et al., an efficient photocatalyst should meet several requirements. An efficient catalyst should be (i) photohydrostable in water, therefore, it must not undergo photocorrosion [19] and (ii) be easily separable from the mixture at the end of the treatment and, therefore, reusable [198]. Moreover, an efficient photocatalyst should be a semiconductor in which the probability of photogenerated electron/hole recombination is very limited. To achieve these objectives it is possible to act as follows: adjust the size and shape of the semiconductor particles; study the positions of the electronic bands and think about the possibility of introducing cocatalysts to limit the recombination of the electron-hole pair; and use sacrificial substances as electron donors [197]. However, when it comes to innovation, it is necessary to refer not only to the performance of the catalyst, and therefore, its efficiency, but above all to the method of synthesis and recyclability [199]. To date, among various semiconductor photocatalysts that can produce hydrogen via the photocatalytic splitting of water, one of the most used semiconductors is TiO₂ as it has the features of superior photocatalytic activity, chemical stability, low-cost and nontoxicity, so it is regarded as a suitable material for use in photocatalytic water splitting for hydrogen production [199].

However, the photocatalytic performance of TiO₂ is influenced by many factors, such as the bandgap, the active facet, the degree of crystallinity, the size, and the morphology. In particular, for anatase TiO₂, the high activity of the (001) facet has been verified to influence the photocatalytic activity, through both theory and experiment [199,200].

If we consider only the TiO₂, the preparation of the anatase TiO₂ materials characterized by an exposed (001) facet is complicated and elaborate. In the literature there is confirmation of this limitation. For example, it is reported that HF in a hydrothermal synthetic process is used to restrain the growth of the (001) facet, and obtain TiO₂ with an exposed (001) facet [200], or hydrothermal or hydrothermal synthesis is envisaged at high pressure. In particular, the use of extremely corrosive and toxic HF or NH₄F is provided as supporting materials for the growing of crystal facets. These are just some examples concerning the synthesis of the semiconductor most used (TiO₂) in the photocatalytic production of hydrogen. However, other obstacles are also faced in the synthesis of other types of photocatalysts. This is the case of MoS₂ [201]. MoS₂ is considered a very good cocatalyst, and it has been experimentally confirmed that hydrogen production on CdS with MoS₂ loading is even more efficient than that of CdS with noble metal loading. However, for

the production of the MoS₂/CdS photocatalyst, the poisonous gas H₂S must be used as a source of sulfur and the calcination temperature is relatively high (above 400 °C [202]).

Another typical difficulty encounter with the heterogeneous powder photocatalyst is the recovery and reuse of the catalyst. The photocatalyst in powder dispersed in the solution. It certainly has interesting advantages: a large specific surface available in contact with the reagents and excellent exposure to light radiation.

Unfortunately, the recovery and reuse of the powder photocatalyst requires an effective separation step which can be quite expensive (e.g., membrane or coagulation/filtration). To overcome this drawback, the solution immobilizes the photocatalysts on macroscopic supports, such as glass beads [203], fiberglass mesh [204], silica [205], alumina, and zeolite [206,207].

Although immobilization makes the photocatalyst recoverable, it reduces the photocatalytic performance due to mass transfer limiting phenomena [208,209]. Alternatively, in order to preserve the advantages of suspended photocatalysts, the ideal would be to synthesize a photocatalyst that is easy to remove after treatment, but which at the same time can work in suspension in aqueous solutions.

The exposed disadvantages limit the development of promising, low-cost and ecofriendly photocatalyst [201]. As for the synthesis method, there are several, but the innovation lies in proposing a short method, with few steps, which does not require the use of harmful and expensive reagents, but which at the same time leads to a photocatalyst with the required characteristics. Consequently, an easy, green, and efficient method is needed for the preparation photocatalyst for hydrogen production. Some of the most significant and (in our opinion) most innovative and environmentally friendly synthesis methods are reported below.

5.1. Noble Metal Free Photocatalyst for H₂ Production

As previously reported, the photocatalytic production of hydrogen is left to all the uses of photocatalytics (based on TiO₂) decorated with noble metals. The presence of noble metal dispersed on the surface of the photocatalyst is important to avoid recombination of the copy with the electron. The most effective catalyst for the reduction in the proton used in the photocatalytic production of hydrogen is Pt, which however, leads to an increase in the cost of hydrogen production and limits its practical application. Therefore, numerous efforts have been made to replace Pt with low-cost alternatives, in which transition metal complexes have also been investigated. Recent studies have shown that interesting results in terms of hydrogen production (under UV or visible light) are also possible for the use of noble metals. The literature proposes the application of metals, such as Ru, Ni, Cu, and Co that present similar efficiencies to that of noble metals, but with a very low cost [210]. Ni is cheaper than noble metals and could represent an alternative giving the interesting characteristics that have led to its use as a cocatalyst combined with semiconductors in photocatalytic processes [184]. Ni at optimal loading of TiO₂ has demonstrated to perform better than Au in photocatalytic hydrogen production [211]. Moreover, relevant amount of molecular hydrogen was found on a Ni-modified perovskite (Ni/La-NaTaO₃), at the optimal nickel load on the surface of the photocatalyst. Indeed the performances of the photocatalyst are strongly influenced by the Ni-load tuning [184]. In the literature low-cost Ni-modified CdS prepared via a hydrothermal reduction method has been proposed for the photocatalytic production of hydrogen starting from lactic acid solution. NiCl₂·6H₂O was used as a precursor, and it was dissolved in 60 mL ethylene glycol to form a light green solution. After that, 200 mg CdS was added. The solution was transferred in autoclave and heated at 200 °C for 10 h. If we consider this method of synthesis, as for all methods that involve “hydrothermal synthesis”, the observation we can make is that, although low-cost materials can be used, the times required for this process are always very long. However, hydrothermal synthesis is a method that allows us to obtain catalytic particles of nanometric dimensions, with very uniform distribution, ideal for heterogeneous photocatalysis applications.

Another interesting proposal reported in the literature is the deposition of Ni on the surface of LaFeO₃, a catalyst confirmed in the photocatalytic production of hydrogen starting from aqueous matrices containing glucose [184]. In this case the LaFeO₃ was prepared with the solution combustion synthesis, a simple and fast method (that requires short times). Ni was photo-deposited in a reducing environment starting from NiCl₂·6H₂O as precursor. The results of the photocatalytic tests showed that Ni improves the photocatalytic hydrogen evolution activity of LaFeO₃ under UV light because it improves the charge separation and transfer. In particular, the H₂ production was approximately 2700 μmol/L after 4 h of irradiation time. This result was also confirmed by the recyclability tests which demonstrated the stability of this catalyst even after 5 cycles. Another recent study on the application of noble metal free photocatalyst for H₂ production, proposes the copper phthalocyanine (CuPc) supported TiO₂ photocatalyst [210]. This photocatalyst is active in the presence of visible light and it has been observed that the amorphous layer of CuPc has the fundamental role of efficiently separating the photogenerated charges and promoting the absorption of light in the visible region. This photocatalyst was prepared with a precipitation method starting directly from CuPc and TiO₂ (P25) in suitable quantities.

In practice, the amorphous CuPc coating layer created on the TiO₂ surface acted as a sensitizer to visible light and also an efficient charge transfer mediator. The idea of using TiO₂ sensitized with dyes for the production of photocatalytic H₂ has been widely reported in the literature. However, in order to free itself from the use of noble metals, research on the use of low-cost transition metal complexes as catalysts for the reduction in protons on TiO₂ has yielded interesting results. This is the case with CoL₂/TiO₂ prepared using cobalt complexes [212]. Co(phen)₂Cl₂Cl and degussa P25 (ass TiO₂) were used for the synthesis. In particular the procedure was a precipitation that provide a step for the filtration and dry in vacuo for 24 h [212].

5.2. Green Synthesis of Photocatalysts for Hydrogen Production

The fundamental point in the production of photocatalytic hydrogen is the synthesis of photocatalysts which have high activities. The catalysts most studied for the production of hydrogen are TiO₂ and all the photocatalysts based on TiO₂, due to their photochemical stability and low cost [213]. Very often, to promote the photocatalytic hydrogen production and to improve the photocatalytic performance of TiO₂, noble metal nanoparticles (NPs), especially Pt NPs, are used as cocatalysts [214]. Indeed, the Schottky barrier formed between Pt NPs and TiO₂ can act as an efficient electron trap to prevent photogenerated electron/hole recombination, and thus promote the photocatalytic reaction [215]. The main need is to produce Pt nanoparticles (or other noble metals) that are uniformly dispersed since the production of hydrogen occurs precisely on the Pt particles. Therefore, it is essential to control the size of the noble metal particles and their distribution. The deposition method for the platinum nanoparticles, and the regulation of their distribution on the TiO₂ surface is the focus of photocatalytic and photoelectrochemical hydrogen production. For most TiO₂/PtNP photocatalytic systems, photodeposition is an efficient and commonly used method [213].

However, among the traditional strategies, most of the reducing and stabilizing reagents used for the synthesis of Pt NP are not compatible with the environment [216,217]. The main drawbacks of Pt NP photodeposition are based on the poor dispersion and morphology of the formed Pt NPs, which is difficult to control in the photodeposition process. Pt growth sites are always randomly distributed, which would lead to nonuniform Pt dispersion and morphology. It is possible to improve this morphological aspect. However, it is necessary to do it with green methods. In this case, green methods for the deposition of metal nanoparticles involve the green synthesis of Pt NP through the reduction in sugars and other biomasses. In this case too, the challenge remains to obtain uniformly dispersed metal nanoparticles. The direct use of biomass to design TiO₂/Pt NP catalysts with precise dispersion and morphology remains a challenge, as well as an opportunity, to open a promising and “green” path for solar to fuel conversion [213]. For example cubic Pt

NPs and spherical Pt nanoclusters were synthesized using wood nanomaterials [217]. In fact natural wood is the most abundant renewable biomass in nature which has attracted growing attention for the preparation of functional materials. The efficient use of this natural resource would be an ideal path for a sustainable approach for future technologies. However, the extraction of cellulose from wood (18) and chemical modifications of cellulose (19) still pose obstacles to the use of wood. It has been shown that nanomaterials derived from natural wood can be used to synthesize Pt NP in aqueous systems with the ability to control particle shapes and sizes with reaction conditions. In this way it is possible to easily prepare spherical and cubic NP Pt supported by wood nanomaterials and spherical Pt nanoclusters [217]. These nanoparticles have been used in the catalytic reactions for the reduction in p-nitrophenol as a model reaction. However, it is possible to transfer the idea of the “green synthesis” of platinum nanoparticles to the TiO₂ used in the photocatalytic reactions of hydrogen production. Therefore, hydrolysis of soluble hemicelluloses can influence the morphology of Pt NPs. Among the most abundant soluble biomasses there is sucrose. In the literature, the use of this biomass is proposed precisely for the chemical deposition of Pt NP on TiO₂. Sucrose was found to be very efficient for forming well dispersed spherical Pt NP cocatalysts. The photocatalysts prepared in this way show higher photocatalytic efficiency than TiO₂/PtNP prepared through the conventional photodeposition process. Furthermore, sucrose could act as an electron donor to generate hydrogen [213]. The synthesis procedure of these spherical Pt NP nanoparticles involved a chemical deposition with the use of chloroplatinic acid (H₂PtCl₆) added to 60 mL of sucrose solution (at different sucrose concentrations) This mixture was then subjected to stirring and heating (100 degrees for 20 min). After heating, the authors observed that the solution had turned brown, which demonstrated the formation of Pt NP. Furthermore, the study carried out showed that the morphology of the Pt NPs formed was mainly related to the sucrose concentrations [213]. Another interesting data reported by the same authors concerned the anchoring contact between TiO₂ and Pt NPs. It plays a key role in the photocatalytic performance of TiO₂ with Pt. In order to obtain TiO₂ catalysts with uniform Pt NP loading, it has been found that the addition sequence of the precursors is also important. Both the TiO₂ suspension and the H₂PtCl₆ were added to the sucrose solutions and heated at the same time. The prepared TiO₂/Pt NP catalysts showed that the Pt NP cocatalysts are well dispersed. Moreover, the surface area of the Pt cocatalysts is a main parameter for explaining the photoactivity behavior of Pt NPs because smaller particles with better dispersity imply higher number of surface-active centers for the photoreactions. In terms of hydrogen production, after 4 h of simulated sunlight, approximately 40 μmol of H₂ has been produced [213].

Another simple, efficient and environmentally friendly way to prepare TiO₂ nanoplates and nanoparticle, which can be applied to H₂-production via photocatalytic water splitting, is the low-heating solid-state chemical method (LSCM) [199]. This method was used to prepare uniform NH₄TiOF₃ nanoplates with a thickness of approximately 100 nm in the absence of surfactants. Solid-solid transformation was used to convert NH₄TiOF₃ nanoplates to TiO₂ nanoplates with an exposed (001) facet via a simple sintering process at different temperatures. The TiO₂ anatase nanoplates obtained in this work have excellent thermal stability. The low heating solid state chemical (LSCM) method, which requires only room temperature or a temperature below 100 C, is an easy, environmentally friendly, and simple method of synthesizing nanomaterials. LSCM has been used to prepare many inorganic nanomaterials, including oxides, sulfides, metals, and composite. NH₄TiOF₃ nanoplates were converted to TiO₂ nanoplates via solid-solid transformation. In particular, an anatase titania was obtained with an exposed 001 facet, without the use of toxic substances, such as HF and NH₄F. The resulting photocatalyst was then used for the production of hydrogen [199]. Typically, this method of synthesis involved 8 mmol of ammonium hexafluorotitanate weighed and ground for 10 min in an agate mortar. Subsequently, 6 mmol of boric acid was added. After grinding at room temperature for 0.5 h, the resulting solid samples were heated in a water bath at 60 °C to perform the entire reaction. The

as-prepared samples were washed with distilled water and dried under natural conditions for 12 h. The final products were fabricated through the calcination of precursor at different temperature. The TiO₂ nanoplates obtained with this method presented a single layer thickness of approximately 50 nm. Moreover, this photocatalyst was characterized by a very good heat-stability, and it was able to withstand high temperatures and maintain a stable anatase phase. The anatase TiO₂ nanoplates exhibit a high H₂ production under different light source (UV and visible), due to the exposed (001) facet and the high crystallinity [199]. Not only TiO₂ but also other types of semiconductors are proposed in the literature for the photocatalytic production of hydrogen. Additionally, for these there is an alternative synthesis, which can be defined green. For example, among these photocatalysts, CdS has received the most attentions, due to its superior light absorption and appropriate conduction-band level [218,219]. However, the CdS, as such suffers from the phenomenon of photocorrosion [220], which can be limited by using a cocatalyst, such as noble metals or tungsten, dispersed on the surface of the CdS [221]. However, the use of noble metals and tungsten is a problem due to their limited availability and their high cost. It is necessary to think of alternative solutions for cocatalysts. An interesting proposal in the literature is MoS₂, for which excellent results are reported in terms of hydrogen production if coupled to CdS, and therefore, used as a cocatalyst. Unfortunately, the problem with MoS₂, as well as for CdS, is the use of the poisonous gas H₂S which must be used as a source of sulfur during the preparation of these two semiconductors, at relatively high calcination temperatures (above 400 °C) [202]. This is a major drawback that has limited the production of two very effective semiconductors. For this reason, and for the principles related to the concept of green chemistry [16], the need arises to find an alternative for the synthesis of MoS₂/CdS photocatalyst, which excludes the use of poisonous substances such as H₂S, but which allows the necessary source of sulfur to be obtained in an ecological way and at a low temperature. In the literature, a hydrothermal synthesis method is proposed for the production of MoS₂/CdS photocatalyst, at a temperature of 200 °C and which uses thiourea as a source of sulfur [201].

For the synthesis CdCl₂·2H₂O (precursor of Cd) and thiourea with the molar ratio of 1:3 were dissolved in 80 mL of deionized water; then in the above solution various quantities of Na₂MoO₄·2H₂O (Mo precursor) have been added. The solution was homogeneously mixed in an autoclave and brought to a temperature of 200 °C for 24 h. Finally, the precipitate obtained was washed with ethanol and water and dried in a vacuum chamber overnight at room temperature. A similar method, always based on the use of thiourea instead of H₂S, was applied for the synthesis of TiO₂/MoS₂/graphene composite used for the photocatalytic production of hydrogen [222]. The loading of MoS₂ enhanced the light absorption of the MoS₂/CdS composite, which would result in higher light energy utilization, and it was observed that the H₂ evolution capability of MoS₂/CdS was 17 times greater than that of CdS. This is certainly a method that allows to obtain a very effective catalyst, a competitive sulfide photocatalysts for efficient solar hydrogen production, but synthesized through an environmentally friendly and inexpensive method.

An effective method for synthesizing photocatalysts for the production of hydrogen from biomass was first reported. Another interesting method to produce photocatalysts in a green way is starting from waste materials. This is the case reported in the literature on the synthesis of Ta₂O₅ photocatalyst prepared started from Ta present in Waste tantalum capacitors.

Waste tantalum capacitors contain approximately 30–40 wt% of rare metal (Ta) tantalum. They are, therefore, one of the main secondary resources of Ta. From these it is possible to recover the tantalum and foresee its reuse for a low-cost preparation as a Ta₂O₅ photocatalyst. It is possible to obtain Ta₂O₅ starting from TaCl₅ used as the precursor for synthesizing Ta₂O₅ by chlorination-sintering process as reported in the literature [223]. To improve the photocatalytic activity, the prepared Ta₂O₅ was further decorated with polyaniline PANI through a simple chemisorption approach. Photocatalytic performance of the samples was evaluated in terms of H₂ evolution and photodegradation of RhB. Polyaniline

(PANI), used to decorate Ta₂O₅, is essential to increase the absorption of visible light by the catalyst. With increasing the PANI content, the visible light absorption of Ta₂O₅/PANI gradually enhanced. It is well known that PANI can absorb visible light. The visible absorption can be related to the electron transitions in PANI from polar on band to *p** band [223]. In particular, with this prepared photocatalyst approximately 200.8 μmol g⁻¹ h⁻¹ of H₂ have been obtained under solar simulated light. Although this is a solution that sees the giving of new life to a waste, the production of a photocatalyst starting from tantalum capacitors to be disposed of consists of various steps. First approximately 10 g of sample must be pretreated by pyrolysis, crushing and screening to obtain particles rich in Ta. Ta-rich particles and FeCl₂ powder with the adding amount of 50% were blended well in a quartz boat and put in a tube furnace, in presence of Argon, AT 500 °C for 2 h. With the chlorination process, Ta was selectively reacted with the chlorinating agent (FeCl₂) and only TaCl₅ was evaporated and collected in the ethanol solution. The TaCl₅ ethanol solution was transferred to a water bath and kept at 70 °C overnight. After being cooled to room temperature, the precipitates were collected by filtration and washed with deionized water. Finally, the precipitates were heated to 700 °C for 6 h under air and approximately 4.12 g of Ta₂O₅ nanoparticles were obtained. The advantage of this method proposed in the literature lies in the fact that it is a method that allows not only the recovery of Ta, but also its transformation into a compound with added value. However, as the authors of the paper rightly state, this recycling technology is valid but is still at the laboratory stage. It is necessary to determine more detailed technical parameters and the true environmental impact of this method (waste and CO₂ emissions). The application of the life cycle analysis to evaluate the potential impact of the whole process on the environment and its sustainable definition compared to other methods is certainly necessary, not only for this method, but for all the proposed synthesis methods defined green.

Another peculiarity required for low-cost and environmentally friendly photocatalyst is their recyclability. The reuse of a photocatalyst for different process cycles is a fundamental requirement to define the sustainable and low environmental impact of photocatalysts. A catalyst is reusable if it can be easily separated from the stream (gas or liquid), in which it is used and above all if it does not lose its performance during the various reuses. The heterogeneous photocatalysts in powder form have the limitation of having to be separated by a filtration method, which will certainly be expensive and limiting in the reuse of the photocatalyst itself. Therefore, the solution supports the photocatalyst on a material that makes it easy to recover and reuse. Specifically, for the H₂ production, there is little information in the literature in terms of supported photocatalyst. As specified above, the immobilization of the active species on a macroscopic support could generate limitations of mass transport phenomena with a consequent reduction in the performance of the process. The solution could be to preserve the advantages of a “suspended photocatalyst” but at the same time it is easy to remove and reuse. An interesting solution proposed in the literature concerns the use of particles with magnetic properties that, coupled with a photocatalyst, form the so called magnetic photocatalyst [224]. The use of this type of support is reported above all for environmental purposes (degradation of contaminants in water) and little has been developed specifically for the production of hydrogen. In any case, the synthesis of this type of supported photocatalyst is certainly very interesting. Magnetic photocatalysts include two components: a magnetic core to make the composite easy to remove by an external magnetic force, and a semiconductor shell with photocatalytic activity under irradiation. Magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃), and M-Fe₂O₄ (where M stands for Ba²⁺, Ni²⁺, Co²⁺, Zn²⁺ divalent metallic cations) are the three most widely used magnetic materials coupled with semiconductors and used as heterogeneous photocatalysts *nostro ferromagnetiche* [225].

Ru-doped LaFeO₃ photocatalyst coupled with magnetic Fe₂O₃ particles was tested in the photocatalytic hydrogen production from glucose solution under visible light irradiation. The catalyst was successfully synthesized by solution combustion synthesis and immobilized on Fe₂O₃ magnetic particles by a physical mixture between Ru-LaFeO₃

catalyst and Fe_2O_3 particles. The physical mixture was dispersed in distilled water and Tetraethyl orthosilicate was added to the solution. The recovered sample was calcined at $450\text{ }^\circ\text{C}$ for 30 min to obtain the Ru-LaFeO₃/Fe₂O₃ composite. The obtained catalyst is easy to recover after treatment, simply by using an external magnetic force. Furthermore, it has shown an excellent performance in terms of hydrogen production starting from aqueous glucose solution (5460 of $\mu\text{mol/L}$ after 4 h of visible irradiation time), but above all an efficient stability having maintained its performances unchanged even after several cycles of use [208]. Therefore, this is a definable “sustainable solution” as it allows to avoid the separation phase by filtering the photocatalyst at the end of the process. Furthermore, the photocatalyst is stable and active in the presence of visible light, which makes the process certainly advantageous from an economic point of view. Other solutions are proposed to immobilize the photocatalytic active phase on macroscopic supports, but such solutions have not yet been applied for the production of hydrogen. However, these are interesting solutions that could also be studied in the photocatalytic production of hydrogen. It is for example immobilization on supports such as glass spheres, quartz flakes, polystyrene pellets [226–228]. The deposition methods proposed are almost always simple and short, which is important for a low-cost and ecofriendly synthesis process. It must be specified that whatever the support is, it must be a material that does not absorb light in order not to compete with the ability of the photocatalytic phase to absorb light. This condition can be overcome only if the support is itself a semiconductor. In this case, a synergistic effect between the photocatalytic active phase and the relative support will be desirable, as reported in the Ru-LaFeO₃/Fe₂O₃ composite case [208].

6. Conclusions

The observation that is certainly needed concerns the nature of the so-called “green” synthesis processes for the photocatalysts. These are certainly interesting processes that allow the production of semiconductors to be adopted in different photocatalytic contexts prepared from waste substances or biomasses, capable of absorbing visible or solar light very well, thanks also to the presence of codopants. The photocatalysts mentioned in this paper are effective for various purposes, from the abatement of pollutants to the production of hydrogen. However, it is believed that in order to define the synthesis of a photocatalyst “green” (whatever its final use), an environmental impact assessment and a life cycle assessment are necessary. From the evaluation of the literature reported in this work, it can be said that the study of ecofriendly and low-cost photocatalyst synthesis focuses more on the efficiency of the synthesis method and the prepared catalyst. No consideration is given to the environmental impact that a preparation method can have with respect to another, especially in the case of low-cost synthesis proposals. However, it must be said that the approaches reported in the literature are absolutely correct, because the proposal of any synthesis method must be justified by the functionality of the photocatalyst and its characteristics, which must respect those required. The photocatalysts prepared with green methods, starting from waste or biomass, must be competitive (in terms of functionality and stability) with the photocatalysts prepared with the classic synthesis methods. The same goes for the choice of codoping, which must be able to significantly enhance the performance of the photocatalysts, otherwise, the choice of using two elements for doping a semiconductor would not make sense. What emerged from this study is the possibility of obtaining promising photocatalysts using alternative synthesis techniques, which can be applied in different contexts.

7. Future Development

Based on the information reported in this review, future research regarding the synthesis methods of heterogeneous photocatalysts will certainly have to include evaluations and insights in terms of LCA between traditional and innovative methods in order to make the choice of innovative methods even more convincing. Moreover, we believe that, in order to consider an innovative photocatalyst, it must be prepared not only with simple proce-

dures, but above all, it must be an environmentally and economically friendly catalyst, and therefore, usable for different process cycles. Experiments are rarely aimed at evaluating the recyclability and stability of a photocatalyst. Another interesting evaluation that could be proposed in future research could be the study of the photocatalytic performance in the degradation of a mix of pollutants (not of a single pollutant, as typically reported in the literature). This could be of strong interest to the scientific community. Formulating a photocatalyst capable of mineralizing a mix of contaminants at the same time means being very close to the real wastewater conditions and therefore, proposing a real and fast application of the photocatalytic process. Therefore, future studies should be carried out on these aspects.

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