

Review

Photosensitive Hybrid Nanostructured Materials: The Big Challenges for Sunlight Capture

Giuseppina Luciani ¹, Claudio Imparato ¹ and Giuseppe Vitiello ^{1,2,*}

¹ Department of Chemical, Materials and Production Engineering, University of Naples Federico II, p.le V. Tecchio 80, 80125 Naples, Italy; giuseppina.luciani@unina.it (G.L.); claudio.imparato@unina.it (C.I.)

² CSGI, Center for Colloids and Surface Science, via della Lastruccia 3, 50019 Florence, Italy

* Correspondence: giuseppe.vitiello@unina.it; Tel.: +39-081-7685975

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Abstract: Solar radiation is becoming increasingly appreciated because of its influence on living matter and the feasibility of its application for a variety of purposes. It is an available and everlasting natural source of energy, rapidly gaining ground as a supplement and alternative to the nonrenewable energy feedstock. Actually, an increasing interest is involved in the development of efficient materials as the core of photocatalytic and photothermal processes, allowing solar energy harvesting and conversion for many technological applications, including hydrogen production, CO₂ reduction, pollutants degradation, as well as organic syntheses. Particularly, photosensitive nanostructured hybrid materials synthesized coupling inorganic semiconductors with organic compounds, and polymers or carbon-based materials are attracting ever-growing research attention since their peculiar properties overcome several limitations of photocatalytic semiconductors through different approaches, including dye or charge transfer complex sensitization and heterostructures formation. The aim of this review was to describe the most promising recent advances in the field of hybrid nanostructured materials for sunlight capture and solar energy exploitation by photocatalytic processes. Beside diverse materials based on metal oxide semiconductors, emerging photoactive systems, such as metal-organic frameworks (MOFs) and hybrid perovskites, were discussed. Finally, future research opportunities and challenges associated with the design and development of highly efficient and cost-effective photosensitive nanomaterials for technological claims were outlined.

Keywords: sunlight harvesting; hybrid nanomaterials; photocatalysts; photosensitive; metal oxide semiconductors; carbon materials; heterostructures; dye sensitization; ligand-to-metal charge transfer; metal-organic frameworks

1. Introduction

Solar energy, as a renewable and low-cost energy source, represents the most reliable and green solution to address energy and environmental issues [1–5]. This has prompted research efforts to effectively harvest and store solar energy into chemical fuels and fine chemicals. With this aim, photocatalytic processes have been developed and employed in different technological fields. Particularly, they exploit semiconductor materials to carry out photo-driven redox reactions for a huge number of applications, such as hydrogen production by water splitting, CO₂ capture and reduction to fuel molecules, pollutants degradation, as well as organic syntheses [4–8]. From a mechanistic point of view, irradiating a photocatalyst by UV/visible light with energy equal or higher than its bandgap, electrons (e[−]) can jump from the valence band (VB) into the conduction band (CB) and leave holes (h⁺), generating electron-hole pairs. These photo-generated charge carriers migrate to the catalyst surface and are then involved in redox reactions (Figure 1a).

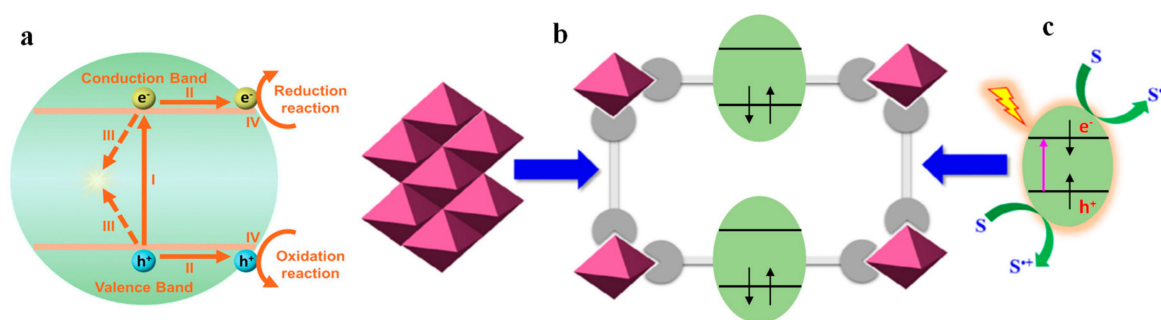


Figure 1. Schematic illustration of the elementary steps of a photocatalytic process involving an inorganic semiconductor photocatalyst (a) or an organic molecule (c). Also, a schematization of the combination between the fundamental units of semiconductor-like nodes and dye moiety containing bridging ligands in photocatalytic hybrid materials (b). Reprinted with permission from [1], Copyright (2019) Elsevier.

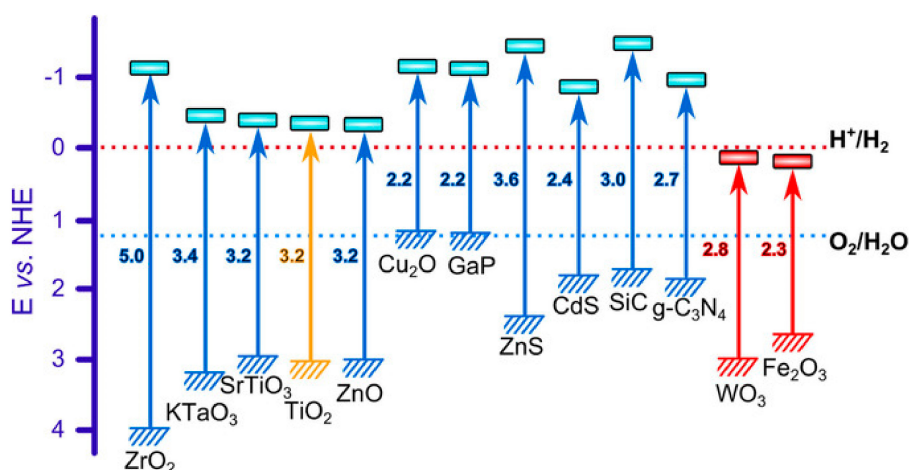
Several parameters determine the performances of a photocatalyst. First, light-absorption properties set the energy of generated excited states, thus driving the reactions with adsorbed species. Furthermore, the recombination of excited electron/hole pairs can occur, limiting the reactivity (Figure 1a). Light absorption by inorganic semiconductor photocatalysts is usually restricted to the ultraviolet (UV) range, and it is hard to extend their absorption features to the visible light range, only through the modification of their structures [6–8]. Also, the charge-recombination phenomena are recurrent. On the other hand, light-harvesting features of organic photocatalysts can be tuned through molecular design. Indeed, the mono-dispersed status of organic molecules endows the intramolecularly separated charges within the discrete organic dyes, to directly transfer out for the destruction and reformation of chemical bonds (Figure 1c) [1]. However, their performances are limited by self-quenching of excited states and photo-bleaching due to their sensitive nature. To overcome these limits, a promising approach, combining inorganic and organic components at the molecular scale, leads to hybrid materials, exhibiting peculiar intrinsic photoelectronic properties and improved photocatalytic performances (as schematized in Figure 1b).

A large variety of strategies to design hybrid materials and nanomaterials with improved photocatalytic activity has been conceived and developed based on (i) the chemical nature of both organic and inorganic components and/or their structural organization and (ii) the different approaches to combine the photoactive molecular species [1–4].

The aim of this review was to describe the most promising strategies for the design and development of hybrid nanostructured materials for efficient sunlight capture and solar energy exploitation in different applications. Specifically, a large class of photocatalysts includes conventional semiconducting oxides, among all TiO_2 , ZnO , SnO_2 , WO_3 , Nb_2O_5 , and ZrO_2 , whose absorption range is limited to the UV radiation, because of their bandgap larger than 3 eV (Scheme 1). Therefore, huge efforts have been made to achieve their photosensitization to visible and possibly even to infrared light. Other interesting oxides, such as Fe_2O_3 and Cu_xO , have a narrower bandgap, but their band potentials maybe not suitable for some reactions, so the formation of hybrid structures can be useful not only to broaden their light absorption but also to tune their energy levels.

The most attractive solutions to improve the photocatalytic performances of oxide-based systems rely on: (i) dye sensitization, (ii) charge transfer complex sensitization, (iii) heterostructures formation, frequently including carbon-based components, and (iv) metal and non-metal doping [7–10]. Doping of TiO_2 and other oxides has already been extensively investigated and reviewed. At the same time, plasmonic nanostructures have been showing an important role in the development of visible light photocatalysts for various applications [11]. In the last few years, huge progress has been made in the coupling of inorganic semiconductors with organic compounds, polymers, and carbon materials, which was the main focus of the present review. In addition, other inorganic-organic hybrid

materials have recently emerged as new types of forthcoming photocatalytic materials, including metal-organic frameworks (MOFs), hybrid perovskites, and semiconducting polymers [1,12,13]. Furthermore, combinations of the previously described systems were explored to enhance photocatalytic performances. This review included the advancements reported since 2015 on all these kinds of hybrid systems for photocatalytic and related applications. Finally, future research opportunities and challenges associated with the development of highly efficient and cost-effective photosensitive nanomaterials for technological claims were envisioned.



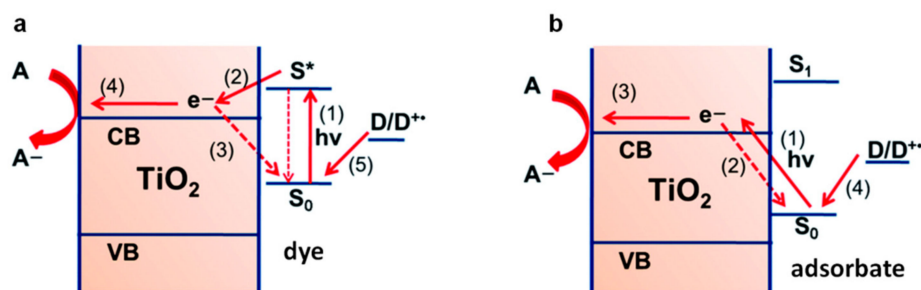
Scheme 1. Bandgap energies, conduction, and valence band positions (referred to the Normal Hydrogen Electrode (NHE) potential at pH 0) of different semiconductors in relation to the redox potentials of water splitting. Adapted and reprinted with permission from [5], Copyright (2017) Royal Society of Chemistry (RSC).

2. Dye Sensitization

A dye is a colored substance that binds to a substrate to give it coloration. Currently, dyes are mostly synthetic and found in a variety of applications, including textiles, leather, food, organic dye lasers, contrast imaging, image sensors, and other optical devices. The use of dye compounds as sensitizers of semiconductors gained interest since the 1960s when the electron transfer from a dye to a metal oxide electrode was recognized as the origin of photoinduced currents in such systems [14]. In the early 1990s, dye-sensitized solar cells (DSCs) started to be developed, especially by Grätzel's group [14], then dyes became widespread in diverse light-harvesting systems. The working principle of *n*-type sensitization is based on the following mechanism: the dye absorbs visible light, exciting an electron from the ground energy state (highest occupied molecular orbital, HOMO) to an excited state (lowest unoccupied molecular orbital, LUMO), then the electron is injected into the conduction band (CB) of the semiconductor (Scheme 2). The cycle has to be completed by restoring the initial state of the dye by means of a suitable electron donor in solution [14,15].

Along with the desired pathway of electron transfer, some processes occur, which contrast the efficiency of the sensitization, generally indicated as recombination processes. The first is direct decay from the excited state, linked to its lifetime. The injected electron may also recombine with the oxidized dye (back electron transfer) or with acceptors in solution. The detailed mechanism of charge transfer is rather complex. It can involve also empty surface states of the semiconductor, and its efficiency depends on both kinetic and energetic factors. The time scale of injection should be largely faster than that of electron decay to the ground state. Then, the electron transport in the semiconductor particle or film should be efficient enough to allow the electron to reach a surface trap, active site, or co-catalyst particle, so it can take part in a redox reaction. The relative position of energy levels at the dye/semiconductor interface (HOMO, LUMO, CB edge, possible surface states) is obviously important, and not straightforward to be experimentally determined, as these energy levels can

depend on the conditions, such as dye-surface interaction and solution environment (pH, dissolved species, etc.). The efficiency of charge transfer and the stability of the photosensitizer/semiconductor system are dependent on the linking mode between the two components. Different interactions can be established, ranging from physical, hydrophobic, and electrostatic interactions to hydrogen and covalent bonding [16,17]. Although physical adsorption is the most used approach, sensitizers bound through weak physical interactions are susceptible to desorption in aqueous solution. Moreover, a stronger interaction with the surface, such as chemisorption or covalent bonding, is generally reported to favor charge transfer. Even ester anchoring bonds formed between carboxyl groups of the dye and surface hydroxyl groups revealed a favorable electronic coupling but also a tendency to hydrolyze under the photochemical reaction conditions [16]. Furthermore, the binding mode and stability are strikingly dependent on solution pH, the concentration of dye and catalyst, and the functional groups of the dye [16,18]. Different types of dyes have been employed as sensitizers. The two main groups are metal complexes and organic dyes, but quantum dots are gaining a growing interest as well. Ruthenium complexes, such as Ru-bipyridyl and Ru-polypyridyl, are the most widely tested dyes, also in solar cells, in order to extend the light absorption spectrum, increase the charge separation efficiency, and enhance the stability of the linkage with the semiconductor [15]. Organometallic complexes of several other transition metals have been studied, e.g., Zn, Sn, Cu, Fe, Co, Os, Ir, Pt. However, some of these metals and the related complex dyes are expensive, including Ru, and some of them imply concerns about their toxicity. Therefore, there is a strong interest in employing metal-free organic dyes, which are usually cheap and exhibit a variety of advantages, especially the possibility to widely control their photophysical properties through structural modifications. For example, the absorption spectra can be tuned by careful consideration of HOMO and LUMO potentials via changing the length of the conjugated system and the electron-donation ability of the donor moiety [15]. Consequently, organic dyes have become the current trend in the field and were considered in this review.



Scheme 2. Schematic illustration of the mechanisms describing (a) dye sensitization and (b) ligand-to-metal charge transfer (LMCT) sensitization for TiO_2 photocatalyst. A and D indicate electron acceptor and donor species, respectively. Adapted and reprinted with permission from [10], Copyright (2014) Royal Society of Chemistry (RSC).

2.1. Organic Dyes in Photocatalytic Systems

Organic dyes can be distinguished in emissive (fluorescent) and non-emissive dyes. Several emissive dyes have a donor-acceptor structure, consisting of three sub-molecular units: an electron-donor group (D), a π -spacer (π), and an electron-acceptor group (A). The D- π -A framework is extensively employed in dye-sensitized solar cells (DSCs) and has also been used in photocatalytic H_2 production systems because it is associated with efficient charge separation, modulation of the intramolecular charge-transfer nature and the absorption properties [15,19]. In this class of dyes, coumarin, merocyanine, triphenylamine, phenothiazine, carbazole, and their derivatives are the most popular electron donor moieties. Some of the principal groups of organic dyes employed as metal-free sensitizers are listed in Table 1. Porphyrins and their analogs, like metal-porphyrin complexes, are found in natural systems: a relevant example are chromophores in chlorophyll, ensuring an efficient solar light harvesting for photosynthesis. This role attracted the interest to implement porphyrins

in DSCs and photocatalytic materials, supported by their wide range of redox, photochemical, and photophysical properties and good photostability. These macrocyclic molecules comprise a rigid two-dimensional 18- π electrons structure (Figure 2), giving high absorption coefficients in two regions of visible light, 400–450 nm (Soret band, blue) and 500–700 nm (Q-bands, red) [16]. Porphyrin- or metalloporphyrin-based nanosystems, either alone, coupled with graphene and semiconductors, or embedded in metal- or covalent organic frameworks (see Section 5) have been studied in photocatalytic processes, such as the reduction of CO₂ to CO, CH₄, or acetylene [20]. Phthalocyanines are structurally related to porphyrins but include more conjugated cycles, extending the Q-band light absorption to near IR, over 800 nm. Similar to porphyrin, the energy of the excited state of phthalocyanines favors the electron injection into the CB of TiO₂; however, they are more rarely investigated as metal-free sensitizers [15].

Table 1. Principal groups of organic dyes used in photosensitization, some relevant members, relative radiation absorption range, and the semiconductors coupled to them reported in this review.

Dye Group	Relevant Dyes	Absorption Range	Semiconductors
Porphyrins	TCPP	400–450, 500–700 nm	TiO ₂ , ZnO, Fe ₃ O ₄
Phthalocyanines		600–800 nm	TiO ₂
Xanthene based	Eosin Y, erythrosin, rhodamine B, fluorescein, rose Bengal	400–600 nm	TiO ₂ , ZnO, SnO ₂ , BiPO ₄ , BiOCl
Anthraquinone based	Alizarin, alizarin red S	400–600 nm	TiO ₂ , ZnO
D- π -A (donor-bridge-acceptor)	Triarylamines, phenothiazines, carbazoles, coumarins (donor groups)	variable	TiO ₂
Cationic dyes	Methylene blue, thionine, Nile blue A	600–700 nm	TiO ₂ , ZnWO ₄
Flavonoids	Anthocyanines, quercetin	580–700 nm	TiO ₂ , ZnO, BiOF

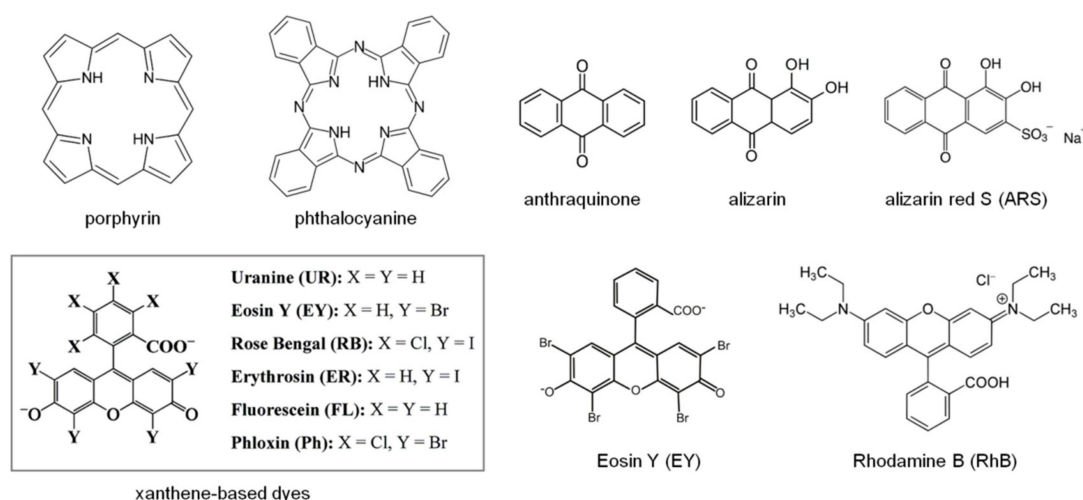


Figure 2. Molecular structures of different dyes commonly employed as sensitizers in photocatalysis. Adapted and reprinted with permission from [15], Copyright (2016) Elsevier.

Xanthene-based dyes are among the most employed in the field of dye-sensitized semiconductors. They typically absorb solar light in the 400–600 nm range and include rhodamine, eosin, erythrosine, fluorescein, rose Bengal, and a variety of derivatives and related compounds (Figure 2). Several advances in the understanding of these dye-sensitization mechanisms have been made, studying xanthene dyes in conjunction with TiO₂ and many other semiconductors. Similarly, some cationic organic dyes, such as methylene blue, thiazole orange, and thionin acetate, have also been found to exhibit photosensitization activity, principally addressing them to the use in H₂ production [15].

Moreover, a variety of natural pigments derived from plants, fungi, or bacteria have been presented, the most common families being flavonoids (especially anthocyanins), betalains, carotenoids,

chlorophylls, tannins, and anthraquinones. Natural dyes are inexpensive, abundantly available, and can be obtained from waste biomass; anyway, their generally low stability suggests the need for protection strategies, e.g., with a conductive layer serving as both a charge transport material and a stabilizer. Several dyes extracted from biomass have been proposed as valid sensitizers in DSCs and in the photocatalytic or photoelectrochemical water splitting, with promising photon-to-current conversion efficiencies [21].

The limited stability under the operative photocatalytic conditions is the main drawback of organic dye sensitization. Most dyes tend to undergo gradual degradation following the electron transfer to the semiconductor, which can represent the first step in the radical mechanisms, leading to partial or complete oxidation of the compound. In fact, dyes are very frequently employed as model contaminants for the evaluation of the photocatalytic oxidation activity of novel materials. On the other hand, the possible sensitization effects, arising from radiation absorption by the dye, may activate different modification or degradation pathways, which might hinder a clear understanding of the action of the photocatalyst [22,23]. The stability of dyes can depend on several factors, besides the nature of the molecule and the catalyst: solution pH, irradiation wavelength and intensity, presence and concentration of suitable electron donors for the regeneration of the dye initial state, and so on. The loading of the photosensitizer itself is another parameter to control, affecting the photocatalytic performance: if the dye concentration is too high, it may tend to aggregate or saturate the semiconductor surface, resulting in activity decrease [16,17]. A larger number of anchoring groups increases the long-term photochemical and linkage stability, which eventually permits higher repeatability of the performances. Lately, many researchers have been making efforts to improve the stability of dyes, primarily through their structural design and the insight into their interaction with the semiconductors.

2.2. Organic Dye-Sensitized TiO_2

Titanium dioxide (TiO_2) is by far the most widely studied metal oxide photocatalyst due to its chemical and photochemical stability, low cost, biocompatibility, and excellent photoinduced activity. It exhibits three primary crystal phases—anatase, rutile, and brookite—stable to ambient conditions. Anyway, its large bandgap (about 3.0–3.2 eV, depending on the crystal phase) and the fast electron-hole recombination are the main limitations to its photocatalytic performances [24,25]. Coupling TiO_2 with dyes is a classical strategy to counteract these issues. Porphyrins and phthalocyanines have been used for the sensitization of TiO_2 , principally as metal complexes, with Zn, Cu, Co, Ru, Sn [15]. However, applications of various metal-free porphyrins were reported in the last years, mainly in the degradation of water contaminants under visible light irradiation. Tetrakis(4-carboxyphenyl) porphyrin (TCPP) was bound on TiO_2 nanoparticles by wet impregnation, giving satisfying and repeatable photocatalytic efficiency, even with 0.1 wt% dye loading [26]. It was suggested that the carboxyl groups anchoring the dye to the surface facilitated electron injection and charge separation lifetime [26]. Many researchers synthesized novel porphyrins, introducing different functional groups with the aim to improve their sensitizing performances. A halogenated porphyrin with 4-chlorophenyl groups (H_2TCIPP) was adsorbed on a photoelectrode made of a TiO_2 nanotubes array [27], two porphyrins with carboxyl-functionalized phenyl groups were anchored to TiO_2 nanorods by a solvothermal procedure [28], hematoporphyrin was combined with N-doped TiO_2 [29], while sulfonated and fluorinated porphyrins with reactive $-\text{SO}_3\text{H}$ groups were conjugated on anatase TiO_2 nanoparticles [30,31]. All these works reported an enhanced visible light activity in the decomposition of dyes or other model pollutants or the inactivation of bacteria. The main properties and best photocatalytic activity results of most reported dye-sensitized systems are summarized in Table 2.

The sensitizer-surface interaction is a crucial point in photoinduced procedures and has recently been studied in detail. The experimental and theoretical investigation of the adsorption of phenylporphyrins on (110) crystal facet of rutile TiO_2 observed a self-metalation reaction, i.e., the formation of Ti-porphyrin complexes (Figure 3) [32,33]. The effect of the anchoring mode of porphyrin derivatives was evaluated by means of surface silanization by APTES (3-aminopropyl triethoxysilane),

allowing an amide covalent grafting on TiO_2 and SiO_2 nanoparticles [34], or surface modification by maleic anhydride of a $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{TiO}_2$ magnetic composite, achieving in both cases stable anchoring and photocatalytic activity [35]. Moreover, using a dimer or trimer of porphyrin with a pyridyl anchoring group, which formed H-bonds on the TiO_2 surface, enhanced both hydrogen generation rate under visible light and stability [36]. A few applications of specifically synthesized metal-free phthalocyanines have also been reported. Different substituted phthalocyanine derivatives were introduced on bare TiO_2 [37,38] or co-doped TiO_2 [39] by hydrothermal or sol-gel process, and an enhanced Cr(VI) reduction or dye degradation was recorded. These are among the rare cases in which the dye is linked to the metal oxide during the synthesis procedure, obtaining hybrid catalysts stabilized by covalent bonds, as reported for a calixarene-based dye introduced in the sol-gel synthesis of porous TiO_2 [40]. In most works, the sensitizers are attached on the surface of nanoparticles by simple adsorption from solution.

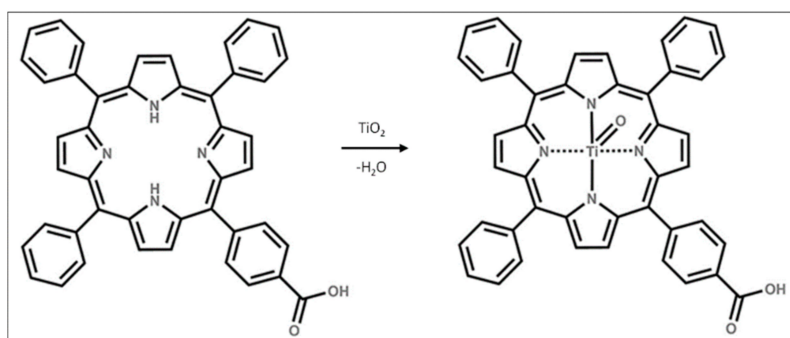


Figure 3. MCTPP (5-monocarboxyphenyl-10,15,20-triphenylporphyrin) and its possible self-metalation product after adsorption on rutile TiO_2 (110) surface. Adapted and reprinted with permission from [33], Copyright (2018) American Chemical Society (ACS).

Xanthene-based dyes include some of the traditionally most widely employed sensitizing organic dyes. Eosin Y (EY), a brominated dye with a benzoic group and an absorption band between 450 and 550 nm, results to be the most widespread in the last years. It was used in combination with TiO_2 for visible light processes, e.g., diclofenac degradation [41] and hydrogen generation, with either Pt [42] or a Co(III) complex [43] as co-catalyst and triethylamine (TEA) as a sacrificial electron donor. Comparable H_2 evolution rates were also obtained on titanate nanotubes modified with Ni [44] and on $\text{TiO}_2\text{-MoS}_2$ photocatalyst [45]. A promising, yet less widely investigated application of photocatalysis is in selective organic synthesis reactions. TiO_2 sensitized by EY was tested in the selective aerobic oxidation of different benzyl ethers to benzoates [46] and of benzylic alcohols to aldehydes [47]. Other systems based on semiconductors different than TiO_2 have employed EY, as described below.

Alizarin (1,2-dihydroxy anthraquinone), a red dye naturally found in plant roots, is another common photosensitizer along with its derivatives, such as alizarin red S (ARS), containing a sulfonate group. Recent papers by Lang, Wang, Hao, and co-workers have dealt with TiO_2/ARS systems for the selective aerobic oxidation of organic sulfides to sulfoxides [48,49], amines to imines [50], and alcohols to aldehydes or ketones [51] under visible light irradiation. Most of these reactions were carried out, taking advantage of TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) as a redox mediator, allowing to achieve excellent yields and selectivities and to improve dye stability (Figure 4). ARS was found to be more efficient than EY, thionine, and Flavin in benzyl alcohol oxidation [51], and than alizarin blue S and nuclear fast red in benzylamine oxidation [50]. The ARS- TiO_2 charge transfer pathway was proposed to be a direct injection rather than the indirect one typical of dyes [49]. The oxidation of sulfides was also performed on anthraquinones-sensitized TiO_2 (alizarin precursors), evidencing the key role of the chelation of Ti ions through the diol group for this family of compounds [52]. $\text{TiO}_2\text{-ARS}$ was successfully tested in another organic synthesis reaction—the cyclization of N,N -dimethylanilines and maleimides to the corresponding tetrahydroquinolines—under visible light irradiation [53].

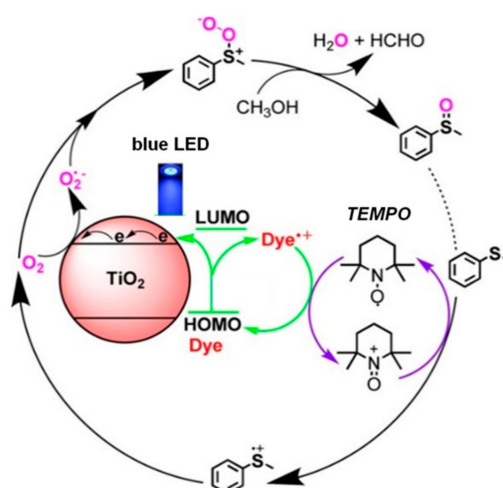


Figure 4. Proposed mechanism for the visible-light-induced selective oxidation of sulfide into sulfoxide with air on alizarin red S (ARS)-sensitized TiO₂ with TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) as a redox mediator. Adapted and reprinted with permission from [49], Copyright (2018) Wiley.

Donor-acceptor (D- π -A) dyes provide plenty of options to tune the electronic and physicochemical characteristics of the molecules by modifying the electron donor, acceptor, or spacer group, or employing multiple donor or acceptor groups. Indeed, several works were devoted to understanding the effect of substituents, functionalities, and alkyl chain size on the photocatalytic efficiency and stability of dye-sensitized TiO₂. All the following cases applied the sensitized photocatalysts for H₂ generation. For instance, in alkoxyphenyl-substituted carbazole dyes [54] and thiophenothiazine dyes [55], the longest alkyl chain gave the best H₂ production rates, thanks to the higher hydrophobicity, extending the charge separation lifetime; in triphenylamine-based dyes, bulkier substituents and additional phenyl donating groups [56] or a thiazolothiazole unit [57] gave higher stability and yields. Phenothiazine-based dyes, featuring thiophene-based spacers and different anchoring groups, have been extensively studied [19], determining an improvement of visible light H₂ generation of Pt/TiO₂ by the effect of the spacer structure [58] and the insertion of a peripheral glucose unit as co-adsorbent (Figure 5) [59]. Other phenothiazine- and carbazole-based dyes were designed for the same application [60], including a D- π -A- π -A photosensitizer, with benzothiadiazole as auxiliary electron withdrawing unit [61], and, in particular, a dibenzopyrromethene (BODIPY)-conjugated phenothiazine, which gave Pt/TiO₂ high activity up to near-infrared (NIR) region [62].

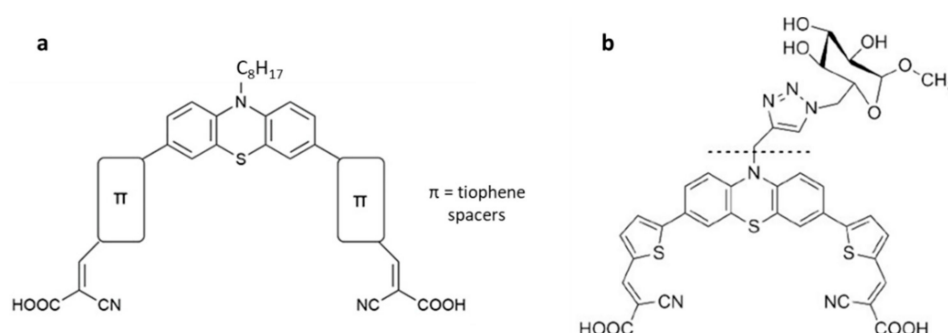


Figure 5. Structure of donor-acceptor dyes with phenothiazine as electron donor, functionalized with an alkyl chain (a) or a glucose derivative (b), thiophene spacers, and cyanoacrylic acid-based acceptor-anchoring groups. Adapted and reprinted with permissions from [58], Copyright (2015) Wiley and [59], Copyright (2018) American Chemical Society (ACS).

Different types of photoactive compounds can be included in the design of a dye with specific structure: some D-A- π -A perylene dyes, featuring cyanoacrylic acid and dicyanomethylene rhodamine as the acceptor/anchoring group, combined with a N-annulated perylene donor and a quinoxaline auxiliary acceptor [63]; two triphenylamine-benzimidazole-based dyes bound on TiO₂, with Cu₂WS₄ nanocubes as an alternative water splitting co-catalyst to Pt [64]; a particular composite dye, consisting of π -conjugated indoline–rhodanine with a chlorophyll derivative, which induced panchromatic absorption in the visible range, efficient electron transfer, and prolonged stability [65]; a series of dyes with triphenylamine donor, vinylthiophene bridge, and a cationic pyridinium acceptor (cationic D- π -A photosensitizers) [66]. A superior H₂ evolution rate was recently reached with a thioalkyl-substituted tetrathiafulvalene dye on mesoporous TiO₂ [67].

Squaraine dyes, based on squaric acid (diketocyclobutenediol), are gaining interest in several applications, including red light and NIR harvesting in DSCs and organic solar cells, owing to their high absorptivity in the region around 600–800 nm and to their easy structure tunability [68]; nonetheless, their use in photocatalytic systems has been limited. Two examples are: a zwitterionic squaraine dye, anchored through π – π interaction to graphene in TiO₂/rGO nanocomposites, active in H₂ production [69], and squaraines featuring dodecyl spacers and carboxylic or phosphonate anchoring groups, coupled with Pt/TiO₂ or Re(I)/TiO₂ to obtain photocatalysts tested in H₂ evolution and CO₂ reduction [68].

As mentioned above, a current trend is a search for effective natural dyes extracted from plants or microorganisms. Recent reports on this kind of dyes as TiO₂ sensitizers include curcumin, a simple conjugated diketone found in turmeric (*Curcuma longa*) [70], and anthocyanin [71]. In several works, natural dyes are extracted from the species containing them, e.g., chlorophyll and flavonoid from parsley leaves and turmeric roots [72], chlorophyll and other pigments from cyanobacteria [73], anthocyanin-rich mixture from *Vaccinium meridionale* Swartz (Andean blueberry) [74], extract from *Picramnia sellowii* tree [75], or *Chlorella pyrenoidosa*, a green unicellular alga used as both sensitizer and biotemplate for Fe₃O₄–TiO₂ composites [76]. Further examples of organic dyes that have been applied in TiO₂ photocatalysis are malachite green (also known as brilliant green) [77] and Sudan black B, a diazo compound [78], for the degradation of polyethylene and phenol, respectively.

Relatively few studies so far have faced the theoretical modeling of the structural and electronic features of the dye-semiconductor interface and its effect on photocatalytic activity. A dedicated DFT investigation considered TiO₂ nanoclusters with different adsorbed dyes: a small rigid molecule based on coumarin, a larger rigid oligomethine cyanine dye with indole groups, and the penicillin V antibiotic, with a flexible backbone [79].

Table 2. Dye-sensitized systems and their photocatalytic activity data under visible irradiation or solar light irradiation. The best results achieved in each work are reported.

Semiconductor	Sensitizer	Preparation	Application	Productivity	Ref.
TiO ₂	TCPP porphyrin (0.05–1 wt%)	Wet impregnation	Rhodamine B (RhB, 10 ^{−5} M) degradation	93% removal after 10 h (90 W)	[26]
TiO ₂ nanotubes array	H2TCIPP porphyrin	Adsorption	RhB (5 mg/L) degradation	93% removal after 4 h (300 W)	[27]
TiO ₂ nanorods	Two substituted porphyrins	Adsorption	4-nitrophenol (10 ^{−4} M) degradation	100% removal in ca. 1 h (400 W)	[28]
TiO ₂ and N-doped TiO ₂	Hematoporphyrin	Adsorption	Methyl orange (MO, 5 mg/L) degradation	33% on TiO ₂ , 88.5% on N-TiO ₂ after 3 h	[29]
TiO ₂ –SiO ₂ core-shell NPs	Carboxy-TCPP, Chlorin e6	Covalent grafting	MO (10 mg/L) degradation	91% removal with Chlorin e6 after 2 h (200 W)	[34]
Fe ₃ O ₄ @SiO ₂ @TiO ₂	Aminoporphyrin	Covalent grafting	RhB (10 ^{−5} M) degradation	96% removal after 1 h (with H ₂ O ₂ , 300 W)	[35]
Pt/TiO ₂ (anatase)	Pyridyl-porphyrin dimer, trimer (30 μ mol/g ca.)	Adsorption	H ₂ production (ascorbic acid solution)	1 mmol/g/h (300 W)	[36]
TiO ₂ (anatase)	Phthalocyanines (H2Pc)	Adsorption	Cr(VI) (10 mg/L) reduction	83%–100% removal in 2.5 h (UV light)	[37]

Table 2. Cont.

Semiconductor	Sensitizer	Preparation	Application	Productivity	Ref.
TiO ₂	Phthalocyanines	Hydrothermal method	Methylene blue (MB, 3 mg/L) degradation	100% removal in ca. 2 h (250 W)	[38]
Co-doped TiO ₂	Phthalocyanine derivative (1 wt%)	Sol-gel	MO (10 mg/L) degradation, Cr(VI) (10 mg/L) reduction	60% MO removal, 71% Cr(VI) removal in 2.5 h (UV)	[39]
Pt/TiO ₂	Calixarene-based dye	Sol-gel	H ₂ production (TEOA solution)	12.2 mmol/g/h (300 W)	[40]
TiO ₂ (P25) on fibreglass	Eosin Y	In situ addition (2 mg/L)	Diclofenac (30 mg/L) degradation	49% removal in 5 min (solar simulator)	[41]
Pt/TiO ₂ (P25)	Eosin Y (7.5–10 wt%)	Adsorption	H ₂ production (TEOA solution)	2.7 mmol/g/h (visible and solar)	[42]
Co complex/TiO ₂ (P25)	Eosin Y	In situ addition (4×10 ^{−5} M)	H ₂ production (TEA solution)	0.45 mmol/g/h ca. (300 W) (TON = 90)	[43]
Ni/TiO ₂ nanotubes	Eosin Y	In situ addition (10 ^{−4} M)	H ₂ production (TEOA solution)	1.2 mmol/g/h ca. (400 W)	[44]
TiO ₂ -MoS _x	Eosin Y	In situ addition (10 ^{−4} –10 ^{−3} M)	H ₂ production (TEOA solution)	1.4 mmol/g/h ca. (solar simulator)	[45]
TiO ₂ (P25)	Eosin Y (0.1 mmol/g)	Adsorption	Benzyl ethers oxidation	100% conv., 71% yield (12 h, visible LED)	[46]
TiO ₂ (anatase)	Eosin Y, others	Adsorption	Benzyl alcohols oxidation	80% yield ca. (1 h, with TEMPO, visible LED)	[47]
TiO ₂ (anatase)	Alizarin red S (0.20 or 0.025 mmol/g)	Adsorption	Sulfides oxidation	80%–90% conv. and sel. (varying time, TEMPO, 300 W or LED)	[48,49]
TiO ₂ (anatase)	Alizarin red S (0.20 mmol/g)	Adsorption	Amines oxidation	90% ca. conv., sel. > 90% (varying time, TEMPO, 3 W)	[50]
TiO ₂ (anatase, P25), ZnO	Alizarin red S (0.025 mmol/g), Flavine, Thionine	Adsorption	Alcohols oxidation	60%–90% conv., 98% ca. sel. (0.5 h, 3 W LEDs)	[51]
TiO ₂ (anatase)	Anthraquinones	In situ addition (0.020 mmol/g)	Sulfides oxidation	80%–90% conv. and sel. (varying time, TEMPO, 3 W LED)	[52]
TiO ₂ (P25)	Alizarin red S, others	Adsorption	Dimethylanilines and maleimides cyclization	91% yield (20 h, 12 W LED)	[53]
Pt/TiO ₂ (anatase)	Substituted carbazole dyes	Adsorption	H ₂ production (TEA solution)	42 mmol/g ca. after 24 h (300 W)	[54]
Pt/TiO ₂	Substituted phenothiazine or triphenylamine dyes (0.1 mmol/g)	Adsorption	H ₂ production (TEOA solution)	70–90 mmol/g ca. after 6 h (400 W)	[55,56]
Pt/mesoporous TiO ₂	Tetrathiafulvalene dyes (0.1 mmol/g)	Adsorption	H ₂ production (TEOA or glycerol solution)	24.5 mmol/g/h (glycerol) (450 W)	[67]
Pt/TiO ₂ (P25)	Triphenylamine dyes (10 µmol/g)	Adsorption	H ₂ production (TEOA solution)	0.2 mmol/g/h ca. (150 W)	[57]
Pt/TiO ₂ (P25)	Phenothiazine dyes (30 or 60 µmol/g)	Adsorption	H ₂ production (TEOA solution)	2.4 or 1.4 mmol/g ca. after 20 h (150 W)	[58,59]
Pt/TiO ₂ film (anatase)	Phenothiazine and carbazole dyes (0.12 mmol/g)	Adsorption	H ₂ production (TEOA solution)	0.14 mmol/g ca. after 24 h (200 W)	[60]
Pt/porous TiO ₂	Phenothiazine dye (30 µmol/g)	Adsorption	H ₂ production (ascorbic acid solution)	90 mmol/g ca. after 10 h (300 W)	[62]
Pt/TiO ₂	Perylene dye (30 µmol/g)	Adsorption	H ₂ production (TEOA solution)	1 mmol/h/g ca. (300 W)	[63]
Cu ₂ Ws ₄ /TiO ₂ (P25)	Triphenylamine dyes	Adsorption	H ₂ production (TEOA solution)	1.4 mmol/g/h (300 W)	[64]
Pt/TiO ₂ (P25)	Chlorophyll-indoline dyad (8 µmol/g each)	Adsorption	H ₂ production (ascorbic acid solution)	4.2 mmol/g ca. after 6 h (350 W)	[65]
Pt/rGO-TiO ₂ (P25)	Squaraine dye	In situ addition (50 µM)	H ₂ production (EDTA solution)	0.040 mmol/h ca. (300 W)	[69]
Pt/TiO ₂ ; Re(I) complex/TiO ₂	Squaraine dyes (20–480 µmol/g)	Adsorption	H ₂ production (ascorbic acid, TEOA or EDTA solution); CO ₂ reduction	4.2 mmol H ₂ /g ca. after 2 h; 0.3 mmol CO/g ca. after 10 h (60 W LED)	[68]
Sol-gel TiO ₂	Curcumin (1–10 wt%)	Impregnation	MB (10 ^{−4} M) and Orange II (2.5 × 10 ^{−5} M) degradation	90% removal ca. after 8 h (18 W)	[70]
TiO ₂ /activated carbon	Anthocyanin (5 µmol/g)	Adsorption	Phenoazopyridine degradation	88% removal in 1.5 h (solar simulator)	[71]

Table 2. Cont.

Semiconductor	Sensitizer	Preparation	Application	Productivity	Ref.
TiO ₂ (anatase)	Chlorophyll, flavonoids	Adsorption	MB (5–15 mg/L) degradation	90% removal ca. after 3 h (150 W)	[72]
TiO ₂ (P25)	Sudan black B	Adsorption	Phenol (5 mg/L) degradation	96% removal in 100 min (400 W)	[78]
TiO ₂ nanotubes	Brilliant green	Adsorption	LDPE films degradation	48% weight loss in 45 days (18 W)	[77]
ZnO	Protoporphyrin, squaraine dye	Adsorption	Acridine orange (5 × 10 ^{−5} M) degradation	70% removal ca. in 1 h	[80]
ZnO nanorods	Fluorescein, protoporphyrin, PTCDA	Adsorption	MB, RhB, Eosin Y, resorcinol (30 or 50 mg/L) degradation	100% ca. removal after 1 h (dyes) or 5 h (resorcinol) (solar simulator)	[81]
ZnO	Curcumin	Precipitation, adsorption	Perylene, fluoranthene, crysene (12 mg/L) degradation	90% removal ca. (varying time, sunlight)	[82]
ZnO	Anthocyanin (0.5 µmol/g ca.)	Adsorption	<i>Escherichia coli</i> (5 × 10 ⁵ cfu/L) disinfection; paracetamol, MB degradation	92% bacteria loss, 70% paracetamol, 80% MB removal (1.5 h, solar sim.)	[83]
ZnO	4ABBN (diazo dye)	Precipitation, sol-gel	H ₂ production (MeOH solution)	102 mmol/g after 4 h (400 W)	[84]
Pt/ZnO nanorods	Eosin Y and rose Bengal	In situ addition	H ₂ production (TEOA solution)	0.52 L/m ² /h after 8 h (300 W)	[85]
ZnO	Alizarin red S	Adsorption	Alcohols oxidation	70%–99% ca. conv. after 7 h (TEMPO, 70 W)	[86]
Sb-doped SnO ₂	Eosin Y	In situ addition (0.1 g/g)	H ₂ production (TEOA solution)	0.25 mmol/h/g (300 W)	[87]
ZnWO ₄	MB	In situ addition (5–15 mg/L)	Cr(VI) (40 mg/L) reduction	97% removal in 45 min (UV-vis, 400 W)	[88]
BiPO ₄ nanorods	Eosin Y (5–30 wt%)	Adsorption	MB, 2,4-dichlorophenol (10 mg/L) degradation	75% MB removal in 80 min, 33% 2,4-DCP removal in 3 h (300 W)	[89]
BiOCl	RhB	In situ addition	RhB, methyl orange degradation	100% RhB removal in 15 min, 90% ca. MO in 2 h (500 W)	[90]
BiOF	Quercetin	Precipitation	Methyl orange, benzotriazole (20 mg/L) degradation	81% MO removal in 1.5 h, 72% BT removal in 9 h (4 × 28 W)	[91]

2.3. Other Organic Dye-Sensitized Semiconductors

Many other semiconducting oxides received the most attention so far in view of their photocatalytic potential and photosensitization. Zinc oxide (ZnO) is one of the most considered, thanks to the suitable properties as very tunable material with high-sensitivity, large specific area, non-toxicity, good compatibility, and high isoelectric point. Also, ZnO showed an excellent chemical stability, as well as a thermal stability, as a *n*-type semiconducting material, favoring a wide range of applications: from photocatalysis to production of solar cells and supercapacitors, as well as luminescent material for biomedical, biosensors piezo-electrics, and optoelectronic devices, in the form of bulk crystal, thin-film, and pellets [92]. However, ZnO nanostructures resulted suitable for absorption in ultraviolet rather than visible light because of the wide bandgap (3.3 eV). Hybrid ZnO was synthesized with organic dye-sensitizers, such as 4-((2-hydroxynaphthalen-1-yl)diazenyl)benzoic acid (4ABBN), by precipitation or sol-gel route, for enhanced H₂ generation from water-methanol solution without co-catalysts [84], as well as curcumin by precipitation, for the degradation of polycyclic aromatic hydrocarbons in daylight conditions [82]. ZnO nanorods with adsorbed fluorescein, perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), or protoporphyrin provided enhanced visible-light degradation of dyes and resorcinol [81]. A ZnO/alizarin red S system was examined in the presence of TEMPO and Ag⁺-Na⁺ electrolyte for the oxidation of aromatic and aliphatic alcohols [86]. Eosin Y and rose Bengal showed a synergistic sensitization of ZnO nanorod array with deposited Pt in H₂ evolution under visible light [85]. Natural dyes, in particular, anthocyanin extracted from Karkade (Hibiscus) flowers, have been associated with ZnO as an effective sensitizer to eliminate *E. coli* bacteria and mineralize their organic components under simulated solar light [83]. Attempts to extend the ZnO sensitization to the

near-infrared (NIR) region have been reported, thanks to conjugation with cyanine dye (IR820) [93], protoporphyrin (PPIX), or squaraine dye (SQ2) [80]. Finally, the interfacial charge transfer between a coumarin dye and ZnO quantum dots was studied by transient absorption and DFT, identifying a rather direct electron transfer mechanism [94].

Zirconium dioxide (ZrO_2) has a bandgap larger than 5 eV, which poses a strong limitation on its radiation absorption range; on the other hand, the highly negative redox potential of its conduction band makes it interesting for photocatalytic reductions. Very few attempts of ZrO_2 sensitization have been reported; a less recent work studied the charge transfer between baicalein, a flavonoid dye, and ZrO_2 nanoparticles, in comparison with TiO_2 [95].

Tin dioxide (SnO_2) is another oxide, which is attracting interest in photocatalysis and photovoltaics (as an electron transport layer in solar cells). Anyway, there are almost no reports about the photosensitization of SnO_2 with organic compounds. Yang et al. demonstrated that Eosin Y was able to sensitize Sb-doped SnO_2 , achieving visible light activity in H_2 production from the TEOA solution with 0.1 g EY/g SnO_2 [87]. Scarce information is available regarding other metal oxides, to the best of the authors' knowledge. Iron oxides show visible light responsivity as a result of their relatively small bandgap; they require modifications to enhance the photocatalytic performances. Anchoring of TCPP porphyrin on Fe_3O_4 nanoparticles was reported to improve the removal of methylene blue (MB), although it appears not clear if that result was to actually correlate to sensitized degradation or prevalently to enhanced adsorption [96].

Some mixed metal oxides have been tested as sensitized photocatalysis as well: zinc tungstate (ZnWO_4) nano rod-like samples prepared by hydrothermal method showed sensitization by methylene blue (MB) in the visible light reduction of Cr^{6+} [88]. Bismuth-based semiconductors have been lately gaining interest: BiPO_4 , BiOCl , and BiOF were sensitized, respectively, by Eosin Y [89], Rhodamine B [90], and quercetin (a natural flavonoid) [91], showing enhanced photodegradation activity under visible light.

3. Ligand-to-Metal Charge Transfer Complexation

Dye sensitization can be regarded as an indirect photosensitization process since it occurs in two steps, starting with light absorption by the dye (Scheme 2). A different sensitization mechanism (type II) has been observed with compounds that do not absorb visible light by themselves but are able to induce an extended light absorption when coordinated with metal ions on the surface of a semiconductor. In this case, the electron transfer occurs in a single step, directly from the ground state (HOMO) of the sensitizing ligand to the conduction band of the semiconductor, without involving an excited state [10,18,97]; hence, the common definition, ligand-to-metal charge transfer (LMCT), or, more in general, molecule-to-band or ligand-to-band charge transfer (Scheme 2).

Several organic compounds, including relatively small molecules, and some metal complexes have been shown to give this kind of direct sensitization when coordinated or sometimes even only adsorbed on the semiconductor. Catechol and its derivatives are the most studied, but also some carboxylic acids, diketones, and inorganic metal complexes (e.g., hexacyanoferrate, $[\text{Fe}(\text{CN})_6]^{4-}$) have shown this property. In principle, when a sufficient degree of electronic coupling is established between the molecular orbitals of the ligand and the CB of the semiconductor, a direct electron injection can occur. These sensitizers have a rather wide HOMO-LUMO gap, which makes the involvement of their excited state in the charge transfer less probable.

The characteristics of LMCT complexes (e.g., binding mode, electronic structure, optical response, charge transfer efficiency, and photochemical stability) are closely related to the chemical structure and electron energy levels of the ligands [10]. The establishment of a strong electronic coupling is favored in case of electron-rich compounds, often containing one or more aromatic rings, with suitable functional groups (e.g., enediol, carboxylate, nitrile, and alcohol) to form stable interactions, such as bidentate coordination, with surface atoms, rather than a mere adsorption [10,18]. These electron-rich ligands tend to determine a large redshift in the absorption edge of wide bandgap semiconductors, usually in

the visible range, reducing their effective bandgap. In this case, the position of the absorption band of the complex depends on the relative energy levels of the ligand's HOMO and the semiconductor's CB edge. It should be underlined that the HOMO and LUMO potentials of organic ligands are not absolute values, but the result to vary according to the semiconductor they are bound to [98,99].

The distinction between type I (indirect) or type II (direct) charge transfer (CT) mechanism occurring in a sensitized system is not always clear and straightforward. Indeed, in some cases, both pathways have a similar probability to be active, even if one can be kinetically favored. In addition, although dyes are commonly associated with indirect CT, some visible light-absorbing molecules are predicted to prefer a direct electron injection [49,69,100]. Direct photosensitization should result in a more efficient electron transfer to the conduction band; on the other hand, the back electron transfer (recombination) might also be favored [97]. Although a stronger electronic coupling is considered to imply a more efficient charge injection, a slightly lower coupling may provide a partially delocalized LMCT, allowing longer charge separation lifetimes and resulting in overall higher efficiency [101]. To date, a limited number of studies have dealt with the detailed evaluation of the electron transfer processes (absorption and emission on the fs-ps timescale) in CT complexes by transient spectroscopic techniques or computational methods.

Semiconductors absorbing only UV radiation, like TiO_2 , happen to show activity under visible light in the degradation of some colorless organic substrates (e.g., phenol, chlorophenols). The reason can be individuated in the LMCT occurring between the substrate, even if only weakly adsorbed, and the photocatalyst. The electron injection from the adsorbate is indeed the first step of its oxidation. The organic radical can accept an electron from a donor in solution, restoring its original form, or it can undergo successive oxidation steps; for example, other electron transfer or the attack by a reactive oxygen species (ROS), eventually leading to its complete degradation [10,18,102]. As a consequence, similarly to dyes, the stability of LMCT sensitizers in the photoreaction conditions may represent an issue that must be carefully evaluated. Nonetheless, these ligands, especially the simplest as catechol, are often reported to be quite resistant to self-oxidation and often added in the reaction system as electron donors, forming CT complexes by in situ adsorption on the semiconductor's surface [103]. Cheap and renewable-derived compounds, e.g., glucose and other saccharides, might be used in this way as sacrificial agents to foster visible light photocatalytic activity.

In the synthesis of hybrid semiconductors with LMCT complexes, various factors have to be taken into account: the type of linking groups of the ligand, the exposed crystal planes of the semiconductor, the accessibility of its metal ions for the coordination, pH of the reaction environment, etc. Bidentate bridging or chelating complexation modes give stronger bonding of the ligand than monodentate coordination, usually reflected in a more efficient and stable CT complex. It should be taken into account that the investigation of the photoinduced CT mechanisms involving small molecules may also turn helpful in the evaluation of the behavior of other compounds with the same structural units or functional groups (dyes and/or polymers), useful for photoinduced applications.

3.1. LMCT-Sensitized TiO_2

The large majority of works on photocatalysts sensitized by direct charge transfer complexes refer to TiO_2 . Catechol (1,2-dihydroxybenzene) and its derivatives are the most extensively studied molecules in the branch of CT complexes. The versatile functions of catechol-based compounds mainly arise from the unique properties and reactivity of the enediol (o-dihydroxyaryl) group, making them ideal bidentate ligands, able to interact with all kinds of surfaces and strongly chelate many transition metals. The adsorption and coordination of catechol and derivatives on the surface of TiO_2 have been studied both experimentally and theoretically, and different binding modes have been proposed, depending also on the considered TiO_2 crystal polymorph and facet (Figure 6a): bidentate chelating, bidentate bridging, monodentate, hydrogen bonding, or mixed configurations [97,104]. The most recent DFT and experimental studies on the structural and electronic characteristics of the TiO_2 /catechol

interaction consider catechol as ligand or anchoring group not only for the application in photocatalytic processes [102] but also for type II dye-sensitized solar cells [104–106].

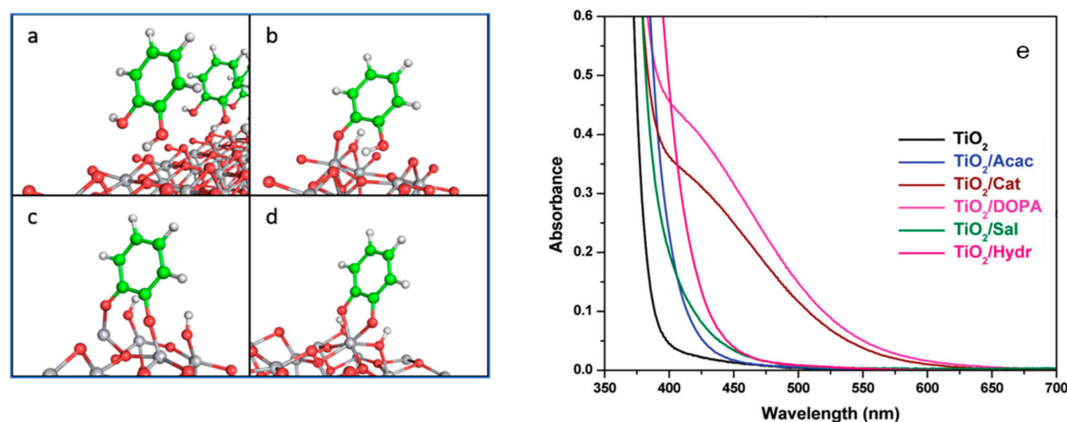


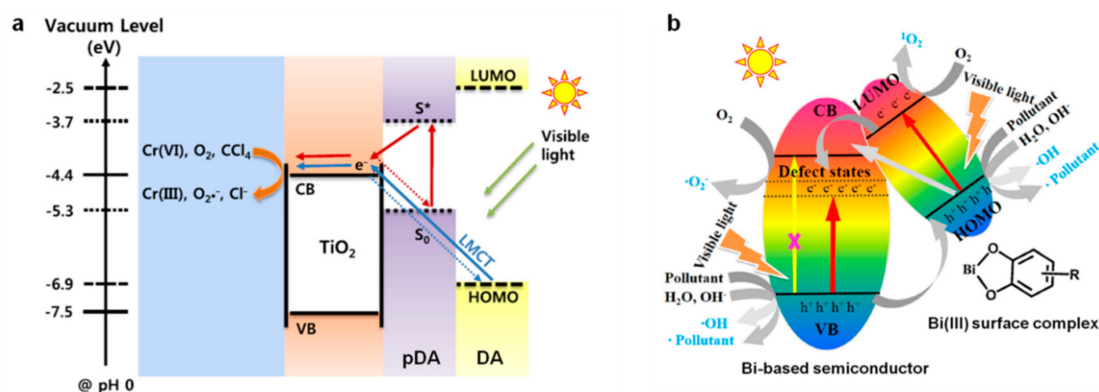
Figure 6. Geometries of Ti-catechol complexes at TiO₂ anatase (101) surface: (a) molecular adsorption, (b) monodentate, (c) bidentate bridging, (d) bidentate chelating coordination; (e) UV-visible absorption spectra of TiO₂ nanoparticles sensitized by acetylacetone (Acac), catechol (Cat), dopamine (DOPA), salicylic acid (Sal), and hydroxamic acid (Hydr). Adapted and reprinted with permissions from [104] and [101], Copyright (2012 and 2016) American Chemical Society (ACS).

Catechol complexation shifts the absorption onset of TiO₂ up to over 600 nm (Figure 6b). The presence of substituents on the catechol ring can enhance the visible light absorption and the photochemical response of the complexes; electron-donating or electron-withdrawing groups are reported to have different effects on the charge separation lifetime and photocatalytic efficiency of the sensitized system [106–109]. For example, electron-withdrawing substituents, such as cyano- or sulfonic groups, fostered H₂ production on Pt/TiO₂ [109]. Other related molecules with enediol functional moiety have been proposed, such as 2,3-dihydroxynaphthalene (or 2,3-naphthalenediol, DHN) [110–113] and ascorbic acid [114]. Salicylic acid [102,113,115,116], as well as the correlated 1-hydroxy-2-naphthoic acid [117] and 5-aminosalicylic acid [116], have shown good sensitization potential, with results comparable to catechol. Interestingly, also glucose, a safe, cheap, and available biomass-derived compound, is able to sensitize TiO₂ [103] or TiO₂/reduced graphene oxide [118] by surface adsorption, allowing visible light activity in Cr(VI) reduction and O₂ reduction to H₂O₂. Monodentate ligands, such as phenol and its derivatives, induced a remarkable extension of the TiO₂ absorption range as well [119]. Even a carboxylate-rich porous carbon obtained by gluconate carbonization on TiO₂ was hypothesized to give visible light activity because of LMCT processes [120].

The main properties of recently reported systems, featuring LMCT complexes and their photocatalytic performances under visible or solar light irradiation, are summarized in Table 3. Despite the number of fundamental and characterization studies, the reports on the photocatalytic properties of such sensitized hybrid materials have started to increase only in the last years. Shi et al. realized the selective oxidation of amines to imines with air on TiO₂ sensitized in situ with different substituted catechols [107] or salicylic acids [115], under blue LED illumination, achieving excellent yields with 0.8 wt% sensitizer, thanks to the cooperation of TEMPO as co-catalyst. Not only oxidation but also reduction reactions were performed by means of sensitized photocatalysts: Fukui and co-workers used TiO₂ impregnated with DHN for the visible-light-driven conversion of aromatic aldehydes to the corresponding alcohols [111] or nitroaromatics to amino aromatics [112]. The visible light activity of the TiO₂ surface modified with 2-naphthol was evaluated in the removal of RhB, As(III) [121], or Cr(VI) [122].

It is interesting to note that most catecholic compounds can undergo oxidative self-polymerization in suitable conditions, such as alkaline pH or light irradiation. For instance, polydopamine is receiving great attention because of its adhesive and hydrophilic properties. Core-shell TiO₂ nanoparticles with

a thin polydopamine layer have been found very active in visible light degradation of RhB [123]. Dopamine and its derivatives norepinephrine and nitrodopamine were polymerized on TiO_2 , inducing visible activity in the removal of pollutants, especially through photoreduction reactions [124]. Contrary to dopamine, complex polydopamine appears to act through a dye sensitization mechanism (Scheme 3a). Even catechol has revealed the ability to polymerize on TiO_2 surface: such sensitized TiO_2 powders were active in Cr(VI) reduction and H_2 production [125], while dip-coated films worked for the inactivation of *Escherichia coli* and *Staphylococcus aureus* in water [126]. Employing polymerized sensitizing ligands should turn out to be an effective strategy to improve the stability of the sensitizer against self-degradation [10,18].



Scheme 3. Illustrations of the electron transfer mechanisms driving visible light photocatalytic activity in (a) TiO_2 -dopamine (DA) and TiO_2 -polydopamine (pDA) systems (LMCT and dye-sensitization, respectively); (b) bismuth-based semiconductors surface-modified by CT complexes with dihydroxyphenyl molecules. Adapted and reprinted with permission from [124,127], Copyright (2017 and 2020) Elsevier.

Other classes of organic compounds have been demonstrated to be capable of LMCT sensitization [10]. Recent reports include: carboxylic acids, such as oxalate [128], amino acids [129], nitrogen heterocyclic compounds, such as pyridine [130], 8-hydroxyquinoline [110,131], and 2-methylisoquinolinium [132], zwitterionic N-substituted aminosulfonic acids [133], or 2-methoxyethanol [134]. Curiously, even apolar aromatic hydrocarbons, lacking the common coordinating functional groups, have exhibited the activation of LMCT with metal oxides: benzene adsorbed on Pd/TiO_2 gave cross-coupling reaction with cyclohexane under visible light, thanks to the activation of a C–H bond [135]. Moreover, acetylene derivatives, such as octyne and ethynylpyrene, used as capping ligands on metal oxide nanoparticles (e.g., TiO_2 , ZnO , RuO_2), create efficient electronic coupling through their π electrons (M–O–C $\equiv$ C– core–ligand linkages) and then interfacial charge delocalization, enhancing sensitized photoluminescence and photocatalytic activity [136].

The peculiar complexation of catecholic compounds on TiO_2 surfaces allows the production of materials with interesting properties besides those directly depending on LMCT sensitization. Dopamine can be used as a powerful and flexible bridge, providing good interfacial contact and charge separation between different components of nanocomposites, as demonstrated for TiO_2 grafted on a glycidyl methacrylate-ethylene glycol dimethacrylate copolymer [137], on N-doped carbon in core/shell nanostructures [138], or melamine-graphene nanocapsules [139]. DOPA (3,4-dihydroxyphenylalanine) and DHICA (dihydroxyindole carboxylic acid) are easily polymerized as conjugated on the surface of oxide colloidal nanoparticles, determining the formation of a Ti-indole LMCT, which induced the oxidative polymerization of monomers to different melanin polymers. The final hybrid TiO_2 -melanin nanostructures have shown excellent antimicrobial activity even without irradiation, owing to their ability in generating reactive oxygen species (ROS) [140–143]. Another interesting family of compounds, yet still poorly studied in the frame of CT complexes, are β -diketones: acetylacetone (2,4-pentanedione) has been shown to considerably shift the absorption onset of TiO_2 [101,144] and ZrO_2 [145] through

LMCT. Moreover, hybrid oxide-acetylacetonate materials prepared by a sol-gel procedure exhibit the peculiar ability to generate and stabilize on their surface the superoxide radical anion (a pivotal ROS), with a consequent activity in organic pollutants degradation even in the dark [144–147]. In most reports, sensitized hybrid materials are prepared by surface adsorption on commercial or synthesized TiO₂ nanoparticles, whereas LMCT sensitized thin films have been seldom investigated, besides some TiO₂ coatings whose surface was functionalized with catechol [126,148]. An alternative preparation method for hybrid bulk materials or films consists of a bottom-up sol-gel route with the introduction of the complexant in a Ti alkoxide solution, obtaining hybrid gels [144] or sols used for dip coating [110] or spin coating [149].

Table 3. Systems sensitized by ligand-to-metal charge transfer (LMCT) complexes and their photocatalytic activity data under visible irradiation or solar light irradiation. The best results achieved in each work are reported.

Semiconductor	Sensitizer	Preparation	Application	Productivity	Ref.
Pt/TiO ₂ (anatase)	Catechol and derivatives (80 µmol/g)	Adsorption	H ₂ production (TEOA solution)	0.60 mmol/g after 5 h (100 W)	[109]
TiO ₂	Catechol and substituted catechols	In situ addition (0.8 mol%)	Amines oxidation	50%–60% conv., >90% sel. in 45 min (with TEMPO, 3 W)	[107]
TiO ₂	Salicylic acid and derivatives	Adsorption, in situ addition (48 µmol/g)	Amines oxidation	90%–98% conv., 98% ca. sel. (varying time, TEMPO, 3 W)	[115]
TiO ₂ (rutile) nanorods	Catechol, salicylic, phthalic, terephthalic acid	In situ addition (25 mg/g)	Catechol, salicylic, phthalic, terephthalic acid degradation (self-sensitized)	15%–20% TOC decrease after 30 min	[102]
TiO ₂ film	Catechol	Impregnation	<i>E. coli</i> , <i>S. aureus</i> (10 ⁵ CFU/mL) inactivation	1000-fold bacteria CFU decrease (10 mW)	[126]
Mesoporous TiO ₂	Catechol (polymerized) (0.5–3.0 wt%)	Adsorption	Cr(VI) (30 mg/L) reduction; H ₂ production (TEOA solution)	100% Cr(VI) removal in 20 min (150 W); 10.9 mmol/h/g H ₂ (solar light)	[125]
TiO ₂ (anatase)	2,3-dihydroxy-naphthalene (0.1–2.5 wt%)	Impregnation	Aldehydes or nitroaromatics reduction	80%–99% conv. (varying time, blue LED)	[111, 112]
TiO ₂	2-naphthol (0.5–2.0 wt%)	Adsorption	Cr(VI) (20–50 mg/L) reduction	100% removal in 1 h (150 W)	[122]
TiO ₂ (anatase)	2-naphthol (0.5–2.0 wt%)	Adsorption	RhB (2 × 10 ^{−5} M) degradation; As(III) (2 mg/L) removal	100% RhB removal in 2 h, 82% As(III) in 1 h (300 W)	[121]
Pt/TiO ₂ (P25)	Ascorbic acid, Zn phthalocyanine	Impregnation, in situ addition	H ₂ production (ascorbic acid solution)	16 mmol/h/g ca. (300 W)	[114]
TiO ₂ (P25)	Glucose, other saccharides	In situ addition (10 ^{−4} –1 M)	Cr(VI) (50–100 µM) reduction; O ₂ reduction to H ₂ O ₂	100% Cr(VI) removal in 40 min; 30 µmol/g H ₂ O ₂ in 2.5 h (300 W)	[103]
TiO ₂ -rGO	Glucose	In situ addition (20 wt%)	Cr(VI) (30 mg/L) reduction	100% Cr(VI) removal in 1 h (150 W)	[118]
TiO ₂ (P25), Pt/TiO ₂ (P25)	Dopamine and derivatives (polymerized)	Self-polymerization	Cr(VI) reduction; As(III) oxidation; O ₂ reduction to H ₂ O ₂ ; degradation of CCl ₄ , dyes, and 4-chlorophenol	100% Cr(VI) removal in 1.5 h; 80% As(III) in 3 h; ca. 200 µmol/g H ₂ O ₂ in 2 h; low dyes and 4-CP removal (300 W)	[124]
TiO ₂ (anatase)	Dopamine, polydopamine	Adsorption, self-polymerization	RhB (10 mg/L) degradation	100% RhB removal in 1.5 h (50 W)	[123]
TiO ₂	Oxalate, other carboxylates, glucose	In situ addition (500 µM)	Ranitidine (100 µM) and other pharmaceuticals degradation	90% ranitidine removal after 6 h (oxalate, 300 W)	[128]
TiO ₂ (P25)	Alanine, glycine, histidine, phenylalanine, serine	In situ addition (100 µM)	Amino acids self-sensitized degradation	Partial mineralization to NH ₄ ⁺ (with peroxymonosulfate, 300 W)	[129]
Pt, Pd, or Rh/TiO ₂ (anatase, rutile, mixed phase)	Pyridine	In situ addition	Pyridine-cyclohexane cross-coupling	3% conv., 99% sel. after 48 h	[130]
TiO ₂ (anatase)	6,7-dihydroxy-2-methylisoquinolinium	Impregnation	Amines photocyanation	96% yield after 3 h (100 W blue LED), 90% after 62 h (51 W IR)	[132]
TiO ₂ (anatase)	Zwitterionic (Good's) buffers	In situ addition (50 mM)	Methyl orange (10 mg/L) degradation	100% removal after 1.5 h (60 W)	[133]
TiO ₂	2-methoxyethanol	Solvothermal process	RhB (20 mg/L) degradation	100% removal after 2.5 h (300 W)	[134]

Table 3. Cont.

Semiconductor	Sensitizer	Preparation	Application	Productivity	Ref.
TiO ₂	Ethynylpyrene	Hydrothermal process	MB (20 mg/L) degradation	100% removal after 15 min (UV)	[136]
TiO ₂ , CaTiO ₃ , BaTiO ₃ , SrTiO ₃	Catechol, salicylic acid, 2,3-dihydroxy-naphthalene	Adsorption	Terephthalic acid (6 mM) oxidation	Increased •OH photogeneration by titanates (150 W)	[113]
ErFeO ₃	Tartrate	Adsorption	MB degradation	100% removal in 1.5 h (UV)	[150]
Nb ₂ O ₅	Toluene	In situ addition	Toluene oxidation (self-sensitized)	18 µmol benzaldehyde after 3 h (200 W)	[151]
BiOIO ₃ , BiOCl, BiOBr, Bi ₂ WO ₆ , Bi ₂ MoO ₆ , BiPO ₄ , Bi ₂ O ₂ CO ₃	Hydroxybenzoic acid and derivatives (25 mg/g)	Adsorption	Hydroxybenzoic acids (20 mg/L) self-sensitized degradation	90% ca. removal after 2 h on BiOIO ₃ (1000 W)	[127]

3.2. Other LMCT-Sensitized Metal Oxides

Very few reports on the charge transfer complex sensitization of other semiconductors for photocatalytic purposes are available. Despite the extensive research on its applications in photocatalysis, zinc oxide has not been the object of much research in this view. Only some studies on the interaction of ZnO with sensitizing ligands were found, e.g., with catechol [152], 1,2-dihydroxynaphthalene, and 8-hydroxyquinoline [131], or dopamine and modified catechol with porphyrins [153]. ZrO₂ and Fe₂O₃ were previously proven to extend their absorption bands following the adsorption of dopamine, ascorbic acid, and alizarin [98]; no recent updates regarding direct sensitization of these oxides were found, although amorphous ZrO₂ complexed with acetylacetone showed absorption extended up to the visible range [145]. Niobium oxide (Nb₂O₅) has been proposed as a photocatalyst as well, and its photoactivity with visible light has been connected with the formation of LMCT with the substrates. This was shown for aromatic hydrocarbons on vacuum heat-treated Nb₂O₅: toluene adsorption under visible radiation leads to its oxidation by a ROS-mediated radical mechanism [151]. Another work reported visible light degradation of 4-chlorophenol and concurrent enhancement of Cr(VI) reduction on Nb₂O₅ nanorods/graphene composite [154]. Titanates, wide bandgap semiconductors with the perovskite crystal structure, also show interesting photocatalytic properties. Studies on the effect of catechol, salicylic acid, and 2,3-dihydroxynaphthalene on interfacial CT on TiO₂, SrTiO₃, and BaTiO₃ have been performed in relation to their band edge potentials [99,113], underlying a broad shift of the absorption onset and enhancement of the photoelectrochemical and photocatalytic properties, not only under visible light but also with UV irradiation. Orthoferrites are less known as perovskite materials in the photocatalysis field; ErFeO₃ functionalized with tartrate ligands was found to show multiple photoluminescence and a considerable photocatalytic activity [150]. Finally, the emerging bismuth-based semiconductors, such as BiOIO₃, were lately investigated with many different dihydroxybenzoic acids as complexing ligands: compounds with an ortho-dihydroxyphenyl structure chelate Bi(III) surface sites forming CT complexes (Scheme 3b) cause the formation of surface oxygen vacancies, affecting the photocatalytic properties over the hybrid semiconductors [127].

4. Carbon-Based Hybrid Nanomaterials

In the last years, carbon-based nanostructured materials, such as graphene and its derivatives [155,156], fullerenes, activated carbons [26,157], biochar [158,159], carbon nanotubes (CNTs) [13,160], and nanoparticles [161], have been of great interest because of their unique structural, electrical, and mechanical properties, offering promising opportunities for photocatalytic applications (Figure 7).

Indeed, carbon-based nanostructured materials can play important roles in the design and synthesis of novel hybrid photocatalysts for different applications [160,162], thanks to a good electron conductivity (related to the characteristic zero bandgap), large surface area, excellent physicochemical stability, and facile synthesis protocols based on a wide variety [163]. Also, the morphologies and crystal structures of carbon-based nanostructured materials can be opportunely defined and produced according to the specific requirements of different applications (Figure 8).

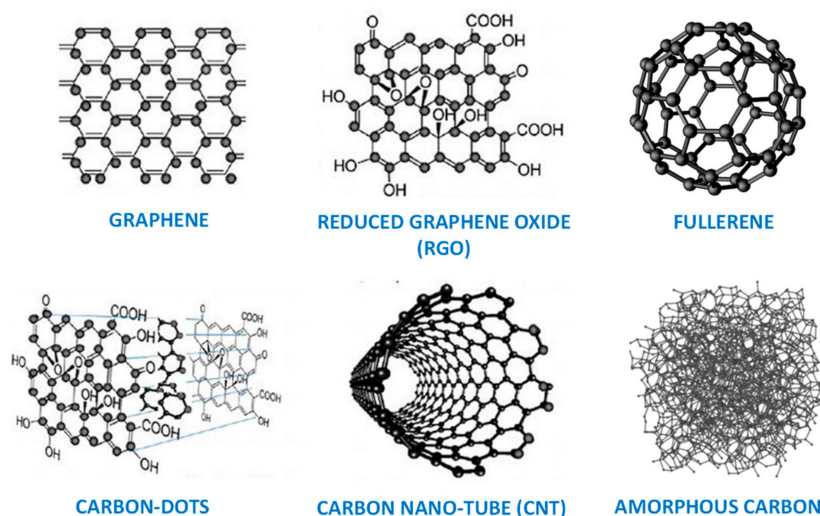


Figure 7. Structure of the most common carbon-based nanostructured materials.

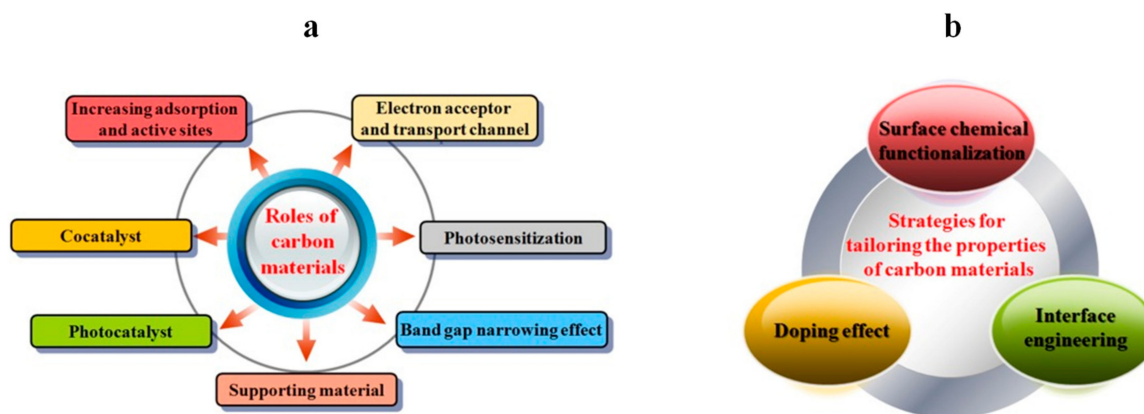


Figure 8. Main roles of carbon-based materials (a) and fundamental strategies for tailoring their photocatalytic properties (b). Adapted and reprinted with permission from [160], Copyright (2016) Elsevier.

The combination of carbon-based nanomaterials with a wide variety of inorganic materials of different sizes, shapes, and compositions leads to hybrid nanostructured materials with tunable catalytic, electronic, optical, magnetic, and redox properties [162]. For example, the vastly increased surface-area-to-volume ratio of catalytic metal oxides or alloy nanoparticles opens new possibilities in electro- and photocatalysis. Such coupling of different nanomaterials has attracted considerable recent attention since the resulting nanohybrids can be potentially applied in many technological areas. Hetero nanostructures of carbon and inorganic materials usually enhance the assets of both components and, due to cooperative effects, can lead to novel functionalities and properties with respect to those of the initial components. Such improvements can reflect in an enhancement of the electrical, thermal, chemical, and/or mechanical properties. In this context, by following different synthetic approaches, carbon-based components have been combined with many inorganic semiconducting oxides, principally TiO_2 and ZnO , as well as BiVO_4 or WO_3 , to produce hybrid nanostructured materials for advanced photocatalytic applications. Indeed, a great number of examples have appeared in the literature, where carbon-based materials have been used as additives of wide bandgap semiconductors, acting either as an electron acceptor or/and sensitizer.

4.1. Carbon-Based/TiO₂ Hybrids

TiO₂, a wide bandgap semiconductor, presents a light absorption limited to the UV region and a very fast charge recombination. In this way, one of the most studied strategies to improve the photocatalytic activity is based on its combination with a carbon-based material (*p*-type semiconductor) in order to induce an enhancement of charge separation yield and extension of the electron lifetime [13]. By following different synthetic approaches, a large variety of hybrid nanostructured materials were recently designed and prepared, combining TiO₂ with different types of carbon-based materials (Figure 9), such as graphene, graphene oxide (GO) [164,165] and reduced graphene oxide (rGO) [69,118,166–168], CNTs [164,169], carbon particles [161,164,170–172], fullerene [169,173], and biochar [158,159,174], working as adsorbers, electron acceptors, and transporters.

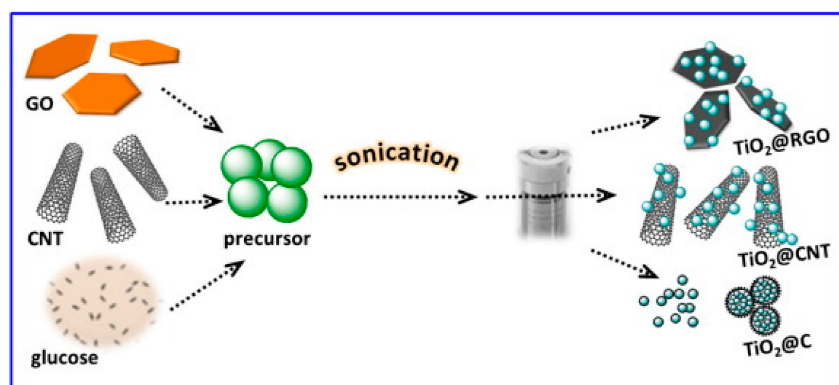


Figure 9. Schematic illustration of the preparation method to obtain carbon-based/TiO₂ nanohybrids. Adapted and reprinted with permission from [164], Copyright (2016) Elsevier.

These hybrid nanostructured materials showed an enhanced visible light absorption, also exhibiting both excellent adsorption capability and photocatalytic activity, for the removal of pollutants [169,175,176] and heavy metal ions from wastewater [177–179], photo-oxidative treatment of organics [167,168,180], as well as water splitting and hydrogen production [178,181–185]. In all cases, hybrid heterostructures have shown a remarkably improved activity, not only due to the bandgap narrowing but also to the large surface area of the hybrid nanostructures in terms of charge transport, proposing them as good photoactive nanomaterials. A summary of the carbon-based hybrid materials considered in this review is reported in Table 4.

4.2. Carbon-Based/ZnO Hybrids

ZnO has been widely considered as a photocatalytic semiconductor. Actually, its photocatalytic efficiency and recycling catalytic utilization efficiency are significantly limited because of the quick recombination of photoelectron-hole pairs. Therefore, improving the photocatalytic and recycling efficiency of ZnO nanostructures is the key to practical photocatalytic applications. Recent research efforts have focused on ZnO-based heterojunctions, enhancing the photocatalytic properties of hybrid nanostructured materials [186–189]. Among them, heterostructures with carbon-based materials have stimulated a very particular interest [188,190]. In this context, many examples of hybrid nanostructured materials have been designed. Particularly, graphene (and its derivatives)/ZnO nanocomposites significantly expand the photocatalytic degradation activity of these host materials [191,192]. Although several methods have been employed to fabricate photocatalytic ZnO nanoparticles adorned with graphene, the synthesis of such nanohybrids with well-ordered particle size without agglomeration for enhanced photocatalytic ability is a challenge. ZnO nanoparticles and graphene can be synthesized by various techniques in order to obtain ZnO nanoparticles decorated graphene nanocomposite for wastewater decontamination. Another important class of carbon-based heterostructures for photocatalysts is constituted by CNTs/ZnO hybrid nanomaterials due to the peculiar molecular

geometry and excellent optoelectronic properties of CNTs [193]. These materials could be tailored to maximize their photocatalytic degradation abilities due to their continuous conducting pathways and extensive interfacial contact. Many ZnO/CNTs heterostructures have been prepared by following different synthetic approaches [193,194], inducing the formation of self-assembly hybrid nanomaterials in which multi-morphology ZnO nanostructures have been tightly combined with CNTs. This approach improved the light absorption efficiency of ZnO nanostructures, as well as the separation efficacy of the photogenerated electron-hole pairs.

Finally, modifications of ZnO photocatalyst with carbon quantum dots (CQDs) have been mostly considered due to low toxicity, aqueous stability, enhanced surface area, economic feasibility, good biocompatibility, and chemical inertness of CQDs [161,172]. Many strategies have been developed to enhance the photocatalytic activity of conventional ZnO via coupling with CQDs, by principally following green and bio-sustainable chemical approaches [195–199]. Therefore, the unique properties of carbon-based/ZnO nanocomposites were used for charge separation, as they reduce the e^-/h^+ pair recombination [200]. The photogenerated e^-/h^+ pairs are involved in oxidation and reduction reactions on the surface of photocatalysts, producing reactive oxygen species (ROS), such as superoxide ($\bullet O_2^-$) and hydroxyl radicals ($\bullet OH$). The formed radicals interact with molecular structures of contaminants, which decompose into less hazardous materials. In all these cases, the use of carbon-based hybrid materials represents the main strategy to enhance the photodegradation of various pollutants in the visible light region. However, the main goal of the researchers is actually focused on the possibility to optimize the particle size and surface area via many easier synthesis methods, in order to make carbon-doped ZnO an exclusive photocatalyst with the use of solar light.

4.3. Other Carbon-Based/Metal Oxide Hybrids

The photocatalytic activity of many other semiconductor oxides was greatly enhanced by conjugation with carbon-based nanomaterials. In this context, iron oxides, such as Fe_2O_3 or Fe_3O_4 , represented promising candidates for the development of visible-light photocatalysis. These oxides were *n*-type semiconductors, with a small bandgap (~ 2 eV), high stability under ambient conditions and aqueous solution at $pH > 3$, low toxicity, and a good tendency to absorb visible light. For example, hematite, Fe_2O_3 , and nanoparticles with large surface area and porous structure have been prepared and revealed distinguished photocatalytic activity. Particularly, hybrid heterostructure of α - Fe_2O_3 with highly hydrophilic carbon dots has been recently reported as a photocatalyst to convert longer-wavelength radiation, e.g., NIR light, into shorter wavelengths, such as visible light, making them of great potential for water splitting [201] and pollutants degradation [202,203]. Similarly, hybrids formed by three-dimensional (3D)-reduced graphene oxide nanosheets containing Fe_3O_4 nanoparticles have demonstrated superior electrochemical performance as supercapacitors electrode [204], as well as graphene/ Fe_3O_4 nanocomposites, showed improved photocatalytic activity [205,206]. Also, Cu_xO -based heterostructures received great attention. For example, nanostructured hybrids with carbon materials, such as CNTs, graphene, C60, carbon quantum dots, carbon fibers, activated carbon, carbon black, have been produced to enhance the performance of Cu_xO photocatalysts for H_2 production by photocatalytic water splitting under visible light irradiation [207–209]. Similarly, carbon-based nanomaterials were combined with tungsten oxides [209,210], indium oxide [211], or bismuth vanadate [212], showing high photocatalytic activity in water splitting or antibiotics degradation.

Table 4. Carbon-based hybrid nanomaterials and their photocatalytic activity data under visible irradiation or solar light irradiation. The best results achieved in each work are reported.

Hybrid Carbon-Based Material	Preparation	Application	Productivity	Ref.
biochar/TiO ₂	Ultrasound-assisted, surfactant-free synthesis	Phenol (50 ppm) degradation; Selective methanol (0.9 vol% in air) photooxidation	64.1% (UV light); 33.6% (visible light); ~80%–90% methyl formate production	[159]
CNTs/TiO ₂ nanostructures	Solvothermal method	Rhodamine B (10 ^{−5} mol/L) removal and degradation (under simulated sunlight)	34.71 mg/g; ~95% after 90 min	[164]
rGO/TiO ₂ nanostructures	Hydrothermal method	Rhodamine B (10 ^{−5} mol/L) removal and degradation (under simulated sunlight)	14.07 mg/g; 100% after 90 min	[164]
Carbon/TiO ₂ nanostructures	Hydrothermal method	Rhodamine B (10 ^{−5} mol/L) degradation (under simulated sunlight)	74.85 mg/g; ~95% after 90 min	[164]
rGO sheet/N, S-CQD/TiO ₂ -P25 nanotubes	Alkaline hydrothermal and physical stirring	Methyl orange (10 ppm) degradation (under visible light)	92% after 4 h	[165]
rGO/TiO ₂ nanotubes	Electrophoretic deposition	CO ₂ conversion to methane (under simulated sunlight)	~6 ppm/cm ² ×h	[166]
rGO/TiO ₂ nanoparticles	Hydrothermal method	Bio-recalcitrant photo-removal	5.093 × 10 ³ ppm TOC/kWh	[168]
Graphene/CQDs/TiO ₂ nanoparticles	Hydrothermal method and physical stirring	Methyl blue (3 ppm) degradation (under visible light)	100% after 90 min	[171]
CQDs/ZnO nanostructured spheres	Microwave-assisted solvothermal synthesis	Photoelectrodes for quantum-dots sensitized solar cells	−1.3 × 10 ^{−4} –8.7 × 10 ^{−5} A/cm ² of current density	[172]
Soot/TiO ₂ nanostructures	Chemical vapor deposition	Rhodamine B degradation (under UV light)	80%	[174]
Carbon/TiO ₂ -P25 nanostructures	Physical mixing under stirring	Air pollutant (5 ppm) removal (under UV light)	47% toluene conversion; ≥60% acetaldehyde degradation	[175]
Graphene nano-platelets/P25-TiO ₂ nanoparticles	One-step hydrothermal method	Methylene blue (0.01 g/L) degradation, NO conversion (under UV light);	~95% after 120 min ~80% after 150 h	[176]
TiO ₂ –In ₂ O ₃ /g–C ₃ N ₄ nanostructures	Solvothermal method	Rhodamine B degradation (under visible light); H ₂ production	~99% 8.6 μmol/h	[178]
N-doped Carbon/TiO ₂	Mixing reaction and thermolysis method	Oxygen reduction reaction	4 μmol NO _x removal	[180]
Exfoliated rGO/TiO ₂ nanostructures	Ionothermal treatment	H ₂ production by water splitting in water–ethanol system	3 mmol/g	[181]
N-doped CQDs/TiO ₂ -P25 nanoparticles	Hydrothermal treatment and physical stirring process	H ₂ production by water splitting using methanol (25 vol%) as sacrificial agent	21.2–58.6 nmol h ^{−1} (under visible light); 2.70–9.80 nmol h ^{−1} (under full-light)	[184]
Au/rGO/TiO ₂ yolk@shell hybrid nanostructures	Precursors reacting in aqueous/organic mixture	H ₂ production by water splitting using methanol as a sacrificial agent; Rhodamine B (2 × 10 ^{−5} mol/L) degradation (under simulated sunlight)	309 mmol h ^{−1} g ^{−1} (visible light); 462 mmol h ^{−1} g ^{−1} (simulated sunlight); ~99.6% after 100 min	[185]
N-doped CNTs/ZnO nanostructures	Homogeneous chemical vapor deposition	Phenol (20 mg/L) degradation (under simulated sunlight)	100% after 20 min	[190]
CNTs/ZnO nanorods	solvothermal synthesis	Rhodamine B (2 × 10 ^{−2} mg/mL) degradation (under simulated sunlight)	90% after 2 h	[193]
CNTs/ZnO nanostructures	Hydrothermal treatment	Rhodamine B (10 mg/mL) degradation (under simulated sunlight)	100% after 2 h	[194]
Lignin-based carbon/ZnO nanoparticles	Solvothermal synthesis	Methyl orange and rhodamine B (15 mg/L) degradation (under simulated sunlight)	99.9% after 30 min; 79.2% after 50 min	[195]

Table 4. Cont.

Hybrid Carbon-Based Material	Preparation	Application	Productivity	Ref.
N-doped C-sheet/ZnO NPs	Hydrothermal treatment	Methylene blue (50 mL) degradation (under UV light)	>95% after 60 min	[197]
ZnO/CQDs nanocomposites	Hydrothermal treatment	Rhodamine B (5×10^{-6} M) degradation (under visible light)	83% within 105 min (annealed at 80 °C); 94% within 105 min (annealed at 200 °C)	[198]
CQDs/ α -Fe ₂ O ₃ nanostructures	Hydrothermal method	Electrochemical performance as photoanodes	2.1 mA cm ⁻² of photocurrent density	[201]
CQDs/ α -Fe ₂ O ₃ nanostructures	Co-precipitation	Indigo carmin (25 mg/L) degradation (under visible light)	100% after 60 min	[202]
Porous g-C ₃ N ₄ / α -Fe ₂ O ₃ nanocomposite	Calcination method	Rhodamine B (10 mg/L) degradation (under visible light)	91.1% after 15 min	[213]
rGO/Fe ₃ O ₄ nanohybrids	One-pot microwave approach	Electrode material for high-performance supercapacitors.	91.4% cycling performance after 190 cycles	[204]
Graphene/Fe ₃ O ₄ nanocomposite	Hydrothermal method	Methyl orange (20 mg/L) degradation (under UV)	99.24%	[205]
rGO/Fe ₃ O ₄ hybrid nanocomposites	Solvothermal synthesis	Methylene blue (12.5 mg/L) degradation (under visible light)	74% after 60 min	[206]
rGO/Cu _x O nanorods	Solvothermal method	CO ₂ conversion to CH ₃ OH (under visible light)	862 mmol g ⁻¹ with rGO/Cu ₂ O; 1228 mmol g ⁻¹ with rGO/CuO	[207]
CQDs/Cu ₂ O heterostructures	One-step ultrasonic method	CO ₂ conversion to CH ₃ OH (under solar-light)	55.7 μ mol g ⁻¹ h ⁻¹	[208]
biomass CQDs/Bi ₂ WO ₆ /Cu ₂ O heterostructures	Hydrothermal method	Tetracycline (20 mg/L) degradation (under visible light)	80% in 90 min	[209]
Carbon layer/In ₂ O ₃ nanobelts	Hydrothermal synthesis	CO ₂ reduction to CO and CH ₄	126.6 μ mol h ⁻¹ ; 27.9 μ mol h ⁻¹	[211]

As summarized in Table 4, a lot of hybrid carbon-based/semiconducting oxides photocatalysts have been designed and developed in the most recent years, by using different synthetic strategies. At the same time, many technological applications have been considered till now; principally, the main claim was the photodegradation of standard organic molecules, such as rhodamine or methylene blue, also showing promising efficiency results. High degradation efficiencies, in the range of 70%–100% and within two hours on average, have obtained in most of the considered studies, strongly depending on the type of produced heterostructure. In this context, the CNTs-based nanohybrids appeared as the most efficient ones, also under simulated sunlight. However, it still appears necessary to hopefully enhance their application in the photodegradation of the most diffuse pollutants in an aqueous environment, i.e., anti-inflammatory and/or antibiotics, to resolve an important environmental question. Also, interesting results have been recently obtained for H₂ production, although many steps forward must be taken to enhance productivity under sunlight.

Finally, an important perspective for the future of this class of hybrid photoactive materials is the possibility to expand the use of bioinspired approach and bio-sustainable sources (i.e., organic wastes) to produce efficient photocatalysts, with the final aim to strengthen the development of green and sustainable chemical processes.

5. Metal-Organic Frameworks (MOFs)

Among organo-inorganic hybrid materials, metal-organic frameworks (MOFs) display very intriguing properties for photocatalytic applications [214]. They are crystalline porous networks obtained, connecting metal-heteroatom clusters and organic ligands through coordination bonds. Also known as porous coordination polymers (PCPs), due to the nature of interaction generating the lattice, these materials show extremely versatile design flexibility as well as modular features. Both

inorganic component and organic ligands can be selected among a huge class of available moieties and assembled, following a lego-like approach, to tailor pores size, light absorption properties, band gap width, as well as nature and number of active sites. Furthermore, their huge surface area and tunable pore size and distribution promote substrate-catalyst interaction, providing at the same time size and shape selectivity towards the desired reaction [1,214,215]. Owing to these superior features, MOFs arise great interest in many photocatalytic processes, including hydrogen evolution [216–218], CO₂ reduction [175,219–221], and pollutant degradation [222–224], as well as organic selective oxidations [225]. In most MOFs, inorganic metal nodes are the active component towards photo-redox reactions, exhibiting photoelectronic properties, typical of inorganic semiconductors (Figure 10a), yet with the better photocatalytic performance [1]. Actually, they can be considered ‘quantum-dot’ semiconductors connected by organic ligands. Due to their nanometric size, charge carriers cover short distances to reach the surface, thus limiting recombination phenomena [1,221]. Furthermore, photo-responsive molecules can be directly employed to build the network, and, due to overlap of electronic states, they can act as molecular antennas to improve visible light-harvesting properties of the semiconductor nodes (Figure 10b), according to a dye sensitizing or a ligand-to-metal charge transfer mechanism (see Sections 2 and 3). Alternatively, organic binders can take part in redox processes through π - π^* transition mechanism (Figure 10c). Finally, the presence of semiconductor nodes and photoactive dye molecules into the same MOF allows dual excitation phenomena of both components, as well as inter-ligand charge transfer, due to the overlapping of frontiers orbitals, thus boosting photocatalytic activity (Figure 10e) [1].

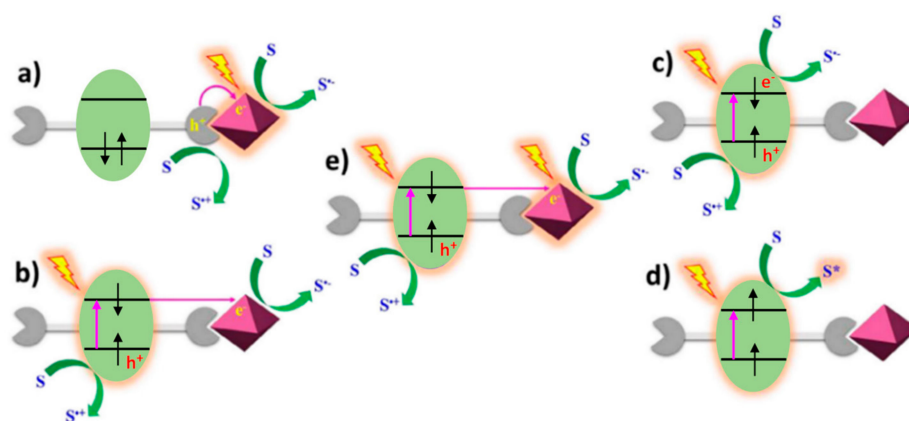


Figure 10. Schemes of photoinduced charge transfer processes occurring in photocatalytic metal-organic frameworks (MOFs): (a) light excitation of a node; (b) light excitation of a photo-active ligand (dye) in semiconductor-type MOF (c) Charge transfer and (d) Energy transfer processes in dye active MOFs; (e) dual excitation phenomena in the presence of semiconductor nodes and photoactive dye molecules into the same MOF [1], Copyright (2019) Elsevier.

Moreover, the presence of a great number of functional groups and coordination sites, as well as porous structure, allow incorporation of foreign photoactive species, metals, or dyes, which further improve photocatalytic properties and confer multifunctionality [1,215,221]. Indeed, despite the huge potential, MOFs performances in photocatalytic processes are still limited by poor absorption in the visible range, as well as charge recombination phenomena. To date, different strategies have been proposed to improve the photocatalytic activity of these systems under solar light irradiation [12,221]. These include: (i) high absorption photoactive ligands, (ii) ligand functionalization, (iii) dye sensitization, (iv) engineering of inorganic building units, and (v) encapsulation of photocatalytic active species (MOF composites photocatalysts). A summary of the most promising strategies and systems developed thereof is reported in Table 5.

Table 5. Strategies to improve metal-organic frameworks (MOFs) photocatalytic activity and performance data of obtained systems under visible irradiation or solar light irradiation. The best results achieved in each work are reported.

Strategy	System/Sample	Application	Productivity	Ref.
High Absorption Photoactive Ligands				
Metalloporphyrins ligands	Cu ²⁺ -PCN224 MOF	Treatment of infected wounds	99.71% against <i>Staphylococcus aureus</i> after 20 min	[226]
Ligands containing specific functional groups (–NH ₂ , –NO ₂ , –SH, and –OH)	Ti(IV)-based MOF (NTU-9)	Rhodamine B (RhB) and methylene blue (MB) degradation	100% after 40 min	[227]
Highly π -conjugated ligands	1,4-bis(2-[4-carboxyphenyl]ethynyl)benzene Zr ₆ O ₄ (OH) ₄ (CO ₂) ₁₂	Methylene blue (MB) and methyl orange (MO) degradation	MB 100% MO 83% after 3 h (higher activity than TiO ₂)	[228]
Tetrakis(4-carboxyphenyl)-porphyrin (TCPP) ligand	(TCPP)—benzoic acid—titanium MOF (PCN-22)	Benzyl alcohol oxidation to benzaldehyde	Conversion 28%; selectivity 100% after 2 h	[229]
Tetrakis(4-carboxyphenyl)-porphyrin (H ₂ TCPP) ligand	zirconium—porphyrin MOF, PCN-222 (also known as MOF-545 or MMPF-6)	CO ₂ reduction	30 μ mol in 10 h	[230]
Bipyridyl ligands	cadmium—organic frameworks Cd(dcbpy) (dcbpy = 2,2'-bipyridine-5,5'-dicarboxylate), Cd(bdc)(bpy) (bdc = 1,4-benzenedicarboxylate; bpy = 2,2'-bipyridyl), and Cd(bdc)(2Me-bpy) (2Me-bpy = 4,4'-dimethyl-2,2'-bipyridyl)	Oxidation of benzylamine	2748 μ mol·g ^{−1} ·h ^{−1} ; 1217 μ mol·g ^{−1} ·h ^{−1} ; 555 μ mol·g ^{−1} ·h ^{−1} ; Selectivity to imine >99% in 7 h	[231]
Imidazolate-Zn(II) charge transfer complex	Zinc-imidazolate MOF (ZIF-8)	Antibacterial	>99.9999% inactivation efficiency	[232]
Metalloporphyrins ligands	Pt ^{II} tetrakis(4-carboxyphenyl)-porphyrin (PtTCPP)—Cu ₂ (COO) ₄ 2D-MOF	H ₂ production	11,320 μ mol g ^{−1} h ^{−1}	[218]
Metal pyridine complexes	Ti-MOF-Ru(tpy) ₂ Ru(tpy): bis(4'-(4-carboxyphenyl)-terpyridine)Ru(II) complex as an organic linker	H ₂ production(photoreforming)	183.3 μ mol·h ^{−1} ·g ^{−1} (triethanolamine as a sacrificial agent, Pt as co-catalyst)	[233]
Mixed ligand	H ₂ TCPP⊂(I-)Meim-UiO-66 (H ₂ TCPP: tetrakis (4-carboxyphenyl) porphyrin, I—iodide ion, Me: methyl, im: imidazolium)	Cr(VI) reduction	13.3 mg _{Cr(VI)} ·min ^{−1} ·g ^{−1}	[234]
Ligand Functionalization				
Amine functionalization	Hierarchical NH ₂ -MIL-125(Ti)	Rhodamine B removal	83% in 2 h	[235]
Amine functionalization	NH ₂ -MIL-125(Ti)	H ₂ production (photoreforming)	60 μ mol·h ^{−1} ·g ^{−1} TEOA as a sacrificial agent	[236]
Amine functionalization	TiO ₂ /1,4-benzenedicarboxylate (bdc) MOF (MIL-125)	Oxidation of benzyl alcohol to benzaldehyde	200 μ mol·h ^{−1} ·g ^{−1}	[237]
Amine functionalization	NH ₂ -MIL-125(Ti)	Oxidation of amines to imines	73% conversion, selectivity towards N-benzylidene benzylamine 86% (in acetonitrile) in 12 h	[238]
Amine functionalization	NH ₂ -MIL-88B (Fe) NH ₂ -MIL-101 (Fe)	Cr(VI) reduction	100% in 1 h	[239]
Amide functionalization	[M(L4) _{0.5} (phen)(H ₂ O)] _n ·2nH ₂ O [M = Zn; Cd] phen = 1,10-phenanthroline	Rhodamine B decomposition	79%–90% in 8 h	[240]
Co–thiolate moieties	Zr-DMBD-Co (DMBD = 2,5-dimercapto-1,4-benzenedicarboxylate)	CO ₂ reduction to CO	3000 μ mol·h ^{−1} ·g ^{−1}	[241]
Covalent organic framework (COF)	Benzoic acid-modified covalent triazine-based frameworks (B-CTF-1) covalently bonded with NH ₂ -MIL-125(Ti) or NH ₂ -UiO-66(Zr) MOFs	H ₂ production	360 μ mol·h ^{−1} ·g ^{−1}	[242]
Rhodamine B (RhB) dye	[Me ₂ NH ₂][Tb ₃ (dcpcpt) ₃ (HCOO)]·DMF·15H ₂ O (Tb-dcpcpt = 3-(3,5-dicarboxylphenyl)-5-(4-carboxylphenyl)-1H-1,2,4-triazole, DMF = N,N'-dimethylformamide)	Nitrofur and quinolone; Antibiotic detection	Nitrofur (99 ppb); Quinolone 1 mM	[243]
Ru(II)-polypyridyl complexes	Ru(bpy) ₃ @MIL-125	Selective oxidative coupling of benzylamines	75% conversion in 3 h	[244]
Erythrosin B dye	Erythrosin B dye sensitized UiO-66 Zr-MOF	H ₂ production (photoreforming)	400 μ mol·h ^{−1} ·g ^{−1} methanol as sacrificial reagent, Pt co-catalyst	[245]

Table 5. Cont.

Strategy	System/Sample	Application	Productivity	Ref.
Engineering of Inorganic Building Units				
Replacement of Zr(IV) to Ti(IV)	NH ₂ -MIL-125(Ti)	Degradation of emerging pollutants (acetaminophen)	100% in 2 h	[246]
Ce(III) doping	Pd/CeMIL-101	H ₂ production from ammonia borane	50,000 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[247]
Encapsulation of Photocatalytic Active Species (MOF Composites Photocatalysts)				
Pt	ZrO ₂ -UiO66-MOF	RhB degradation	100% in 40 min	[248]
Pd	Pd@Cu(II)-MOF	Benzyl alcohol oxidation reaction	Conversion 93%–99%; Selectivity >99% (to benzaldehydes)	[249]
Pt	Calixarene-sensitized Pt@UiO-66-NH ₂	H ₂ production (photoreforming)	1528 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ methanol as sacrificial reagent	[250]
Pt/Au	M-doped NH ₂ -MIL-125(Ti) (M = Pt and Au)	H ₂ and HCOO [−] production	Pt-MOF H ₂ : 562 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ HCOO [−] : 32.5 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$; Au-MOF H ₂ : 100 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ HCOO [−] : 8 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[251]
Cu deposited and encapsulated	Cu/Cu@UiO-66	Oxidation of benzyl alcohol	49.50%	[252]
Ni	Ni ^{II} (bpet)(H ₂ O) ₂]@Ru-UiO-67 (Ni@Ru-UiO-67)	CO ₂ reduction to CO	196.8 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[253]
Re ^I (CO) ₃ (BPYDC)Cl, BPYDC = 2,2'-bipyridine-5,5'-dicarboxylate + Ag	Ag ₃ Re ₃ -MOFRe ^I (CO) ₃ (BPYDC)Cl, BPYDC = 2,2'-bipyridine-5,5'-dicarboxylate linked to a zirconium MOF, UiO-67 (Re _n -MOF)	CO ₂ reduction	Turnover number (TON) $1.4 \times 10^{-2} \text{ h}^{-1}$	[254]
C ₃ N ₄	g-C ₃ N ₄ /ZIF-8	CO ₂ reduction; H ₂ production	CH ₃ OH production 0.75 $\mu\text{mol h}^{-1} \text{ g}^{-1}$, 309.5 $\mu\text{mol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$; TEOA as a sacrificial reagent	[255]
TiO ₂ hollow nanospheres (HNSP)	double-shell TiO ₂ @ZIF-8 hollow nanospheres	H ₂ production	254.2 $\mu\text{mol h}^{-1} \text{ g}^{-1}$ (TEOA, methanol as sacrificial reagent)	[256]
TiO ₂ nanofibers	TiO ₂ nanofibers with NH ₂ -UiO-66	CO ₂ reduction	0.8 $\mu\text{mol h}^{-1} \text{ g}^{-1}$	[257]
Titanate nanotube (TNTs)	BUC-21/TNTs BUC21: bis-1,3-dibenzyl-2-oxo-4,5-imidazolidinedicarboxylic acid—Zn ²⁺ 2D MOF	Cr(VI) reduction and adsorptive Cr(III) removal	99% in 40 min	[258]
TiO ₂	TiO ₂ @NH ₂ -MIL-88B(Fe)	Cr(VI) reduction	100% removal in 25 min	[259]
BiOBr nanosheet	NH ₂ -UiO-66/BiOBr NH ₂ -MIL-125(Ti)/BOBr	Tetracycline hydrochloride (TC) degradation and Cr(VI) reduction;	TC decomposition and Cr(VI) removal: 75% in 120 min;	[260]
		Norfloracin (NOR) degradation	NOR removal efficiency 93.6%	[261]
Ag ₃ VO ₄ , Ag ₂ WO ₄	IL-125-NH ₂ / Ag ₃ VO ₄ Ag ₂ WO ₄	Methylene blue (MB) and rhodamine B (RhB) degradation	90% MB removal; 100% RhB removal in 60 min	[262]
CdS	CdS/ZIF-8	CO ₂ reduction to CO	CO evolution 93.3 $\mu\text{mol h}^{-1} \text{ g}^{-1}$	[263]
MoS ₂	MoS ₂ /ZIF-8	Ciprofloxacin (CIP) and tetracycline hydrochloride (TC) degradation	CIP 95%; TC 80% in 180 min	[264]
CH ₃ NH ₃ PbI ₃ (MAPbI ₃) perovskite QDs	MAPbI ₃ @PCN-221(Fe _{0.2})	CO ₂ reduction	1559 $\mu\text{mol g}^{-1}$; CO ₂ converted to CO (34%) and CH ₄ (66%)	[265]
Activated carbon (AC)	AC/MIL-88B (Fe)	Reactive Red198 (RR198) degradation	99% in 30 min	[266]
rGO	rGO-Zr-based UiO-66(NH ₂)	Cr(VI) reduction	100% in 100 min	[267]
rGO	MIL-53(Fe)	Cr(VI) reduction; RhB degradation	Cr(VI) 100%; RhB 83% in 80 min	[268]

5.1. High Absorption Photoactive Ligands

Using ligands with highly efficient light absorption as organic building blocks is the most effective approach to increase light-harvesting properties and decrease charge recombination phenomena. Notably,

high photo-responsive ligands in the visible light range include porphyrins/metallo-porphyrins [226,269], moieties containing specific functional groups ($-\text{NH}_2$, $-\text{NO}_2$, $-\text{SH}$, and $-\text{OH}$) [227], conjugated systems [228], as well as metal complexes [12]. Obtained systems are usually active under visible light irradiation, allowing higher performance than bare TiO_2 under UV-light excitation. Porphyrins, metallo-porphyrins, and metal complexes have been widely employed to build MOFs with efficient visible light harvesting. MOF PCN-22, obtained by assembling Ti–O carboxylate clusters with tetrakis(4-carboxyphenyl)porphyrin (TCPP), shows a wide absorption range from 200 nm to 640 nm, as well as a narrow bandgap (1.93 eV). Similar features are disclosed by zirconium-porphyrin MOF, PCN-222, (also named as MOF-545 or MMPF-6). In both systems, the dye acts as an antenna for the metal nodes (Figure 7) and allows both high charge separation and intensive light absorption. This results in high photocatalytic yield under visible light conditions (Figure 11), even higher than those measured on UiO-66- NH_2 and MIL-125- NH_2 under similar conditions [229,230].

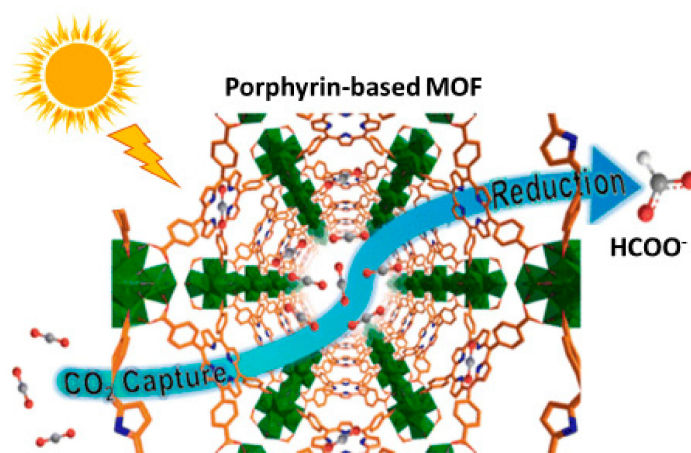


Figure 11. The activity of porphyrin-based MOF towards CO_2 capture and reduction. Adapted and reprinted with permission from [230], Copyright (2015) American Chemical Society.

Bipyridyl-containing cadmium–MOFs, $\text{Cd}(\text{dcbpy})$ show high light-harvesting properties as well as high activity and selectivity towards photo-oxidation of benzylamine to *N*-benzylbenzaldimine under visible light irradiation at room temperature, without any photosensitizer or co-catalyst [231]. Actually, they show higher activity than conventional inorganic semiconductors, such as TiO_2 , Nb_2O_5 , WO_3 , even doped with noble metals, under similar conditions. Ligand-to-metal charge transfer mechanism enables MOFs photoactivity under solar irradiation. This occurs in zinc-imidazolate MOF (ZIF-8), disclosing high antibacterial activity and huge potential in air pollution remediation and personal care (Figure 12) [232]. Antibacterial performance of ZIF-8 is far higher than highly active photocatalysts MOF MIL-100(Fe), NH_2 -MIL-125(Ti), and NH_2 -UIO-66(Zr) in photoinduction.

Metal conjugation to aromatic ligands markedly enhances their intrinsic visible light absorption [12]. Introducing Cu^{2+} cations into the porphyrin ring of porphyrin Zr MOF PCN 224 boosts light absorption at 660 nm and, at the same time, hinders electron-hole recombination, ultimately enhancing photocatalytic yield. Obtained systems can be efficiently employed as antibacterial formulations in wound healing [226]. Notably, single Pt atom coordinated porphyrin has been employed as a ligand to produce MOF nanosheets with an impressive H_2 production rate of $11,320 \mu\text{mol g}^{-1} \text{h}^{-1}$ through water splitting under visible range [218]. Similarly, a Ru(II) complex with bis(4'-(4-carboxyphenyl)-terpyridine), $(\text{Ru}(\text{tpy})_2)$, has been exploited for the synthesis of Ti-Ru(tpy) $_2$ MOF, which shows intensive absorption and, consequently, enables photocatalytic hydrogen production through photoreforming in the visible light region [233].

Organic ligands, containing unsaturated carbons and conjugated species, can also play a key role in modulating the bandgap and, consequently, MOFs' photocatalytic properties. As a proof of concept, using π -conjugated 1,4-bis(2-[4-carboxyphenyl]ethynyl) benzene (cpeb) as a linker for

$\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$ clusters leads to a Zr-based MOF (VNU-1) with absorption edge in the visible range, at about 540 nm, and higher photocatalytic activity than Degussa P-25, as well as UiO-66(Zr) and UiO-67(Zr) MOFs, with the same structure [228]. Similarly, 2,5-dihydroxyterephthalic acid employed as a linker to build Ti-based MOF NTU-9 significantly influences both the valence band (VB) and the conduction band (CB), resulting into a wide absorption in the visible range up to 750 nm and small bandgap (1.72 eV) [227].

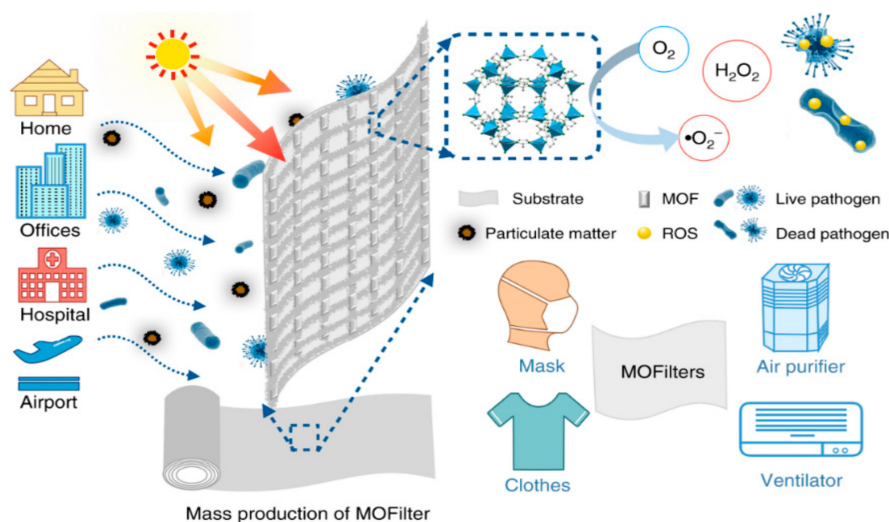


Figure 12. Schematic illustration of metal-organic framework (MOF)-based filter (MOFilter) for integrated air cleaning. Adapted and reprinted with permission from [232], Copyright (2019) Springer Nature.

An effective approach to design highly photoactive MOFs consists in the simultaneous use of two or more linkers. This strategy is useful to include bulky metalloorganic ligands [12] into the framework and allows tuning porosity and functions of obtained MOFs. The mixed-ligand strategy was applied to incorporate porphyrin into an imidazole-functionalized Zr-based MOF, enlarging visible absorption up to 750 nm [234]. A mixed linker Zr-MOF was also synthesized by assembling 2D layers, composed of Zr_6 clusters and primary linker benzene tribenzoate (BTB), with TCPP porphyrin. The obtained MOF revealed a 3D layer-pillar structure, intensive absorption in a wide range of the solar spectrum, as well as high photocatalytic activity towards diclofenac degradation [270].

5.2. Ligand Functionalization

MOFs photo-electronic properties can be improved by the modification of organic ligands. This can be carried out either during synthesis in-situ or following a post-synthetic approach [12,242]. Actually, electron-donating/withdrawing features of substituting groups influence the energies levels of both valence and conduction bands and, consequently, optical features as well as redox potentials. Furthermore, they can also affect charge recombination phenomena. As a general rule, electron-donating substituents can extend the absorption range to the visible light region, thus promoting photocatalytic performance [12]. Notably, semiconducting features are strongly influenced by the resonance effects in the organic ligands [271]. Among the investigated substituents, a huge number of studies prove the great efficacy of amino groups in extending MOFs absorption to the visible range. Particularly, amino-functionalized Ti-MOFs, including $\text{NH}_2\text{-MIL-125}(\text{Ti})$, disclose high performance in a great number of photocatalytic processes, including water purification [235], H_2 production [236], CO_2 reduction [272], as well as organic synthesis [237,238].

Recent studies proved that, under light irradiation, photogenerated electrons could migrate to Ti nodes, whereas holes are localized on the amino group (Figure 10b); this hinders charge recombination and promotes photocatalytic performance [273]. In amino-functionalized Fe-based MOFs, the ligand to metal electron transfer mechanism coexists with charge separation phenomena in semiconductor

Fe-O clusters under visible light (Figure 10e), concurring to impressive photocatalytic activity towards CO_2 as well as Cr(VI) reduction [12,239]. Adding a higher number of amino functional groups can further shift the light absorption of MOFs to longer wavelengths, but it decreases the oxidation power due to the shift of VB potential to more negative values [274].

As reported by recent studies, even amide functionalization can improve photocatalytic properties [240]. Moreover, ligand functionalization can be carried out to anchor metal ions with catalytic activity. In this way, Zr-based MOFs were modified, including thiol groups that acted as binding sites for Co(II) ions. Obtained Co-thiolate moieties acted as co-catalysts toward efficient and selective CO_2 reduction under visible light [241]. A novel promising approach to produce visible-light responsive MOFs consists of post-synthesis covalent modification with a covalent organic framework (COF). This strategy was successfully applied to $\text{NH}_2\text{-MIL-125}(\text{Ti})$ or $\text{NH}_2\text{-UiO-66}(\text{Zr})$ systems, which were modified with triazine-based frameworks (B-CTF-1). Compared to bare MOFs and even physical mixtures of MOFs and COFs, obtained MOF/COF hybrid materials showed higher stability, as well as hydrogen production rate, due to the presence of amide bonds between B-CTF-1 and MOFs, ensuring wide absorption range as well as long-lived photogenerated charge carriers [225,242], as shown in Figure 13.

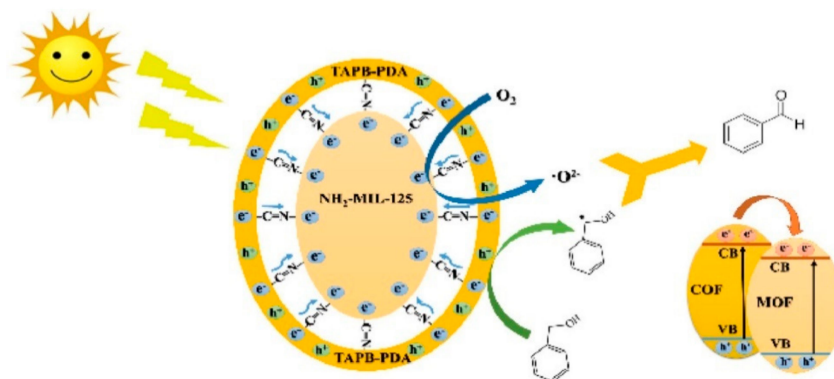


Figure 13. Scheme of bonding features and electronic properties of MOF/COF (covalent organic framework) hybrid materials and their involvement in the photooxidation of aromatic alcohols. Adapted and reprinted with permission from [225], Copyright (2020) Elsevier.

The coating of $\text{NH}_2\text{-MIL-125}$ with shell via a covalent bond linkage modifies the intrinsic electronic properties and reduces the recombination rate of photogenerated electron-hole pairs, resulting in excellent performances. Introducing a dye into the semiconductor-like network usually shifts its absorption edge to the visible range and further improves the photocatalytic activity. This approach can be implemented through post-synthesis conjugation using amino groups in the ligand [243]. Following this strategy, Ru(II) -polypyridyl complexes were inserted into MIL-125 MOF, obtaining a stable system with high photoactivity for the selective oxidative reactions of amines [244]. As a more promising alternative, dye sensitization can be carried out during the synthesis process (in-situ strategy). Following this approach, erythrosin B dye was included in Zr-based MOFs (UiO-66), which were not active in the visible range. Contrarily, obtained dye-sensitized Pt-UiO-66(Zr) systems showed enhanced photocatalytic activity towards H_2 production under visible light, owing to the charge transfer from excited erythrosin to the MOF and subsequent electron migration to Pt NPs [245].

5.3. Engineering of Inorganic Building Units

MOFs photocatalytic properties can be also tuned through an accurate design of the inorganic cluster. Notably, metal ion substitution in the inorganic node can improve light harvesting and depress charge recombination phenomena, thus enhancing photocatalytic performance. In this regard, partial replacement of Zr with Ti atoms in $\text{NH}_2\text{-MIL-125}(\text{Ti})$ MOF results in high activity for remediation of pharmaceutical pollutants under solar irradiation [246].

Ce(III) doping into the MIL-101(Cr) network promotes charge migration through $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox pair and allows hydrolysis of borazane under visible light [247]. Alternatively, in MOFs-based semiconductors, even the size of inorganic building blocks can be exploited as a parameter to tune photoelectronic properties. Notably, larger assembling units account for smaller band gaps and allow photocatalytic response in the visible region [12].

5.4. Encapsulation of Photocatalytic Active Species (MOF Composites Photocatalysts)

Encapsulating metal, metal-containing species, or carbon nanomaterials into MOF frameworks can further improve their photocatalytic properties and is currently considered one of the most promising strategies to design high-performance photocatalysts. Actually, MOF nanocomposites combine the advantages of both host nanostructures (optical, catalytic, electrical, magnetic, etc.) and MOFs matrix (high surface, tunable ordered structure, etc.), present multifunctional behavior, and often unravel unique properties due to intimate interaction between the components. Noble metal nanoparticles (MNPs) play a key role in enhancing MOFs photocatalytic properties [1]. Intrinsic properties of MOFs, such as high surface area, allow fine dispersion of MNPs and avoid their aggregation. Due to surface plasmon resonance (SPR) effects, MNPs can improve visible light absorption. Moreover, they can accept photogenerated electrons, thus limiting charge recombination [1,221], ultimately leading to superior catalytic performance.

Pt nanoparticles can be deposited on ZrO_2 -based MOF by atomic layer deposition (ALD), increasing the photocatalytic activity. This could be ascribed to the promotion of charge separation phenomena and limitation of electron/hole recombination [248]. A combination of photoactive ligands with MNPs significantly further promotes photocatalytic performance. This occurs in UiO-66- NH_2 and even in MIL-125(Ti)- NH_2 MOFs, whose already relevant properties can be improved by encapsulating Pd [249], Pt [250], or Au [251]. Accepting photogenerated electrons from inorganic semiconductor clusters, Pt and Au can also act as co-catalysts in redox processes [272]. As an alternative to noble metal nanoparticles, doping with less expensive metals, such as Cu, can also significantly enhance both stability and photocatalytic activity, as a result of the plasmonic phenomenon and metal-semiconductor junction, improving charge mobility and depressing recombination (Figure 14) [252].

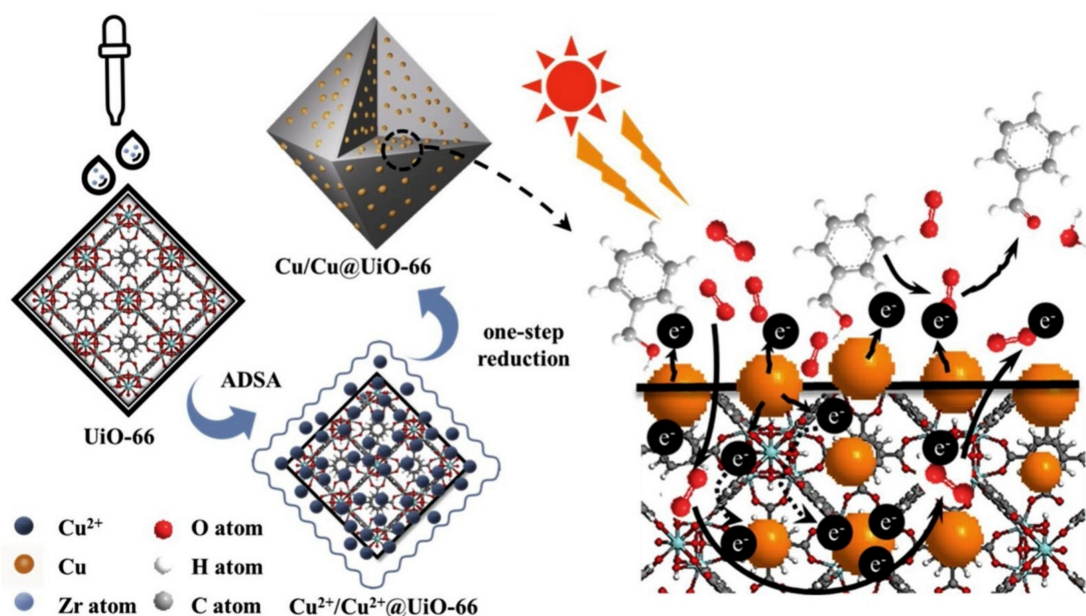


Figure 14. Scheme of the synthesis approach of Cu@UiO-66 composite and reaction mechanism for partial oxidation of benzyl alcohol under visible light irradiation. Adapted and reprinted with permission from [252], Copyright (2019) Elsevier.

Active metal species can be also encapsulated as molecular catalysts to enhance MOF photocatalytic efficiency. In this regard, Ni@Ru-UiO-67, as well as Ag@Re-UiO-67, systems showed efficient CO₂ conversion to CO under visible light [253,254].

Another valid approach to reduce charge recombination rate and improve MOFs photocatalytic performance is based on their coupling with semiconductor nanoparticles, such as TiO₂, ZnO, CdS, C₃N₄ [255]. Cu(II)-porphyrin and TiO₂ nanoparticles into MOF structure (PCN-224(Cu)) leads to a marked improvement of light-harvesting features and promotes separation of photogenerated charges, reaching superior photocatalytic performance for CO₂ reduction [219,256]. Also, composites or heterostructures of titanium oxide or titanate fibers and MOFs, such as TiO₂@NH₂-MIL-88B(Fe), disclose high photocatalytic activity [257–259]. Recently, novel heterojunctions, based on bismuthoxyhalide-MOFs composites, were successfully produced by controlled growth of BiOX (X=Cl, Br) nanosheets on the surface of NH₂-UiO-66 and NH₂-MIL-125 (Ti). These composites showed impressive photocatalytic activity under solar irradiation due to the absorption of visible light, as well as the efficient charge separation and transfer at the interface between BiOX and MOF components [260,261,275]. Less conventional nanostructures, such as silver vanadate (Ag₃VO₄) and silver tungstate (Ag₂WO₄) nanoparticles, can be included in Ti-containing MOF (MIL-125-NH₂) to enhance its photocatalytic performance, which proved even better than previously investigated samples [262]. CdS, as well as MoS₂, have been raising great interest for photocatalytic processes due to their low bandgap (around 2.4 eV) that enables activity under visible light, but they suffer from poor stability caused by photo-corrosion. Their inclusion into a MOF framework, however, allows a fine dispersion of nanoparticles, avoids aggregation, improves stability, promotes sunlight absorption and photo-generated electron-hole exchange between the components, and ultimately improves photocatalytic activity [263,264].

Similarly, including lead halide perovskite quantum dots (QDs) into Fe-porphyrin-based MOF confers stability in water-containing systems. Furthermore, the close interaction between QDs and the Fe catalytic site in the MOF allows the fast exchange of photogenerated electrons, enhancing the photocatalytic activity towards CO₂ reduction, which was 38 times higher than on the bare components [265]. Apart from inorganic semiconductors, integrating MOFs with conductive carbon materials is an effective approach to promote the migration rate of photogenerated carriers [12,221]. For example, composites obtained combining activated carbon (AC) with MIL-88B (Fe) MOF showed higher photocatalytic activity than bare components [266]. Furthermore, reduced graphene oxide (RGO) can be coupled to MOF frameworks, such as UiO-66(NH₂) [267] and RGO-MIL-53(Fe) [268] to improve their photocatalytic properties. Interestingly, incorporating both semiconductor nanoparticles, such as CdS quantum dots, and RGO nanosheets into a MOF appears as a promising strategy to (i) expand absorption properties of the MOF to visible light, (ii) match heterojunction bandgap, (iii) allow selective adsorption to enhance catalytic activity, (iv) protect CdS nanoparticles from leaching. All these features promote sunlight harvesting, photo-generated charge migration, as well as selectivity and, as a result, the photocatalytic activity [223]. As a general rule, the interfacial between MOFs and nanostructures, semiconductors, and RGO in MOF nanocomposites plays a key role in defining the photocatalytic behavior.

Certainly, many strategies for MOFs design have been developed (as summarized in Table 5) to increase the photocatalytic activity under visible irradiation or solar light irradiation. Several applications have been considered: significant performances (in the range of 80%–100% after not-long time) have been shown in the photodegradation of organic dyes, while promising H₂ productivity values (between 0.75–10000 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) have been obtained. Therefore, new approaches must be explored to design heterojunctions with intimate interaction and bandgap matching with the aim to increase the photocatalytic activity.

6. Conductive Polymers-Based Hybrid Nanomaterials

Conductive polymers are very interesting organic macromolecules, widely considered for the design of advanced hybrid materials with photocatalytic properties [276], thanks to their good

processability, especially through solution processes [277]. Conductive polymers can provide matched band structures with other inorganic semiconductors, such as metal oxides nanostructures, reducing the recombination of photogenerated electron-hole pairs for obtained hybrid composite photocatalysts [278,279]. More specifically, the loading of conductive polymers improved the photostability of semiconductor photocatalysts, also inhibiting their photo-corrosion. At the same time, the presence of π -conjugated long chains in the conductive polymers makes them able to trap the photoinduced holes, thus hindering the self-oxidation of the same photocatalysts. On the other hand, a conductive polymer combined with a semiconductor photocatalyst has shown different roles under different light irradiation: under UV-visible light irradiation, the conductive polymer can act as a co-catalyst, which is excited by irradiated light and a hole transporting material, while under visible light irradiation, only the conductive polymer can be excited as a photosensitizer [277,279]. The most used conductive polymers, which have been loaded into various semiconductor metal oxides, are polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT), and polythiophene (PTh), schematized in Figure 15.

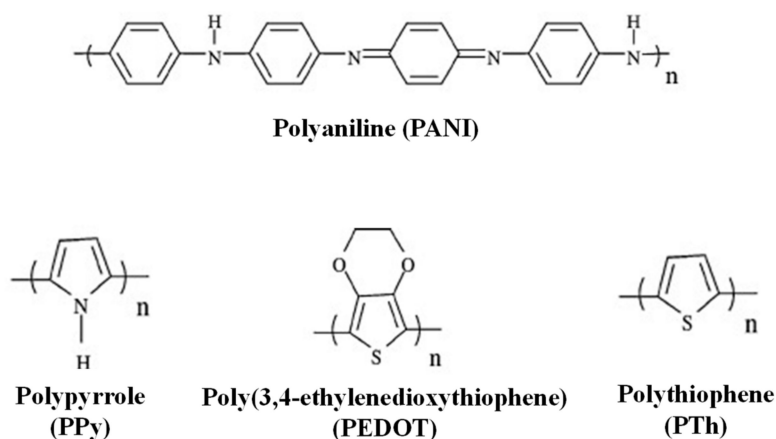


Figure 15. Molecular structures of the most used conducting polymers combined with the semiconducting metal oxides.

Many different nanostructured materials have been systematically produced by using various preparation methods, determining different morphologies and photocatalytic performances. Particularly, the combination of conductive polymers and semiconductor metal oxides determined an enhancement in the separation of photoexcited charge carriers, also extending the light absorption range, increasing the adsorption of reactants (Figure 16), inhibiting photo-corrosion, and reducing the formation of large aggregates. Consequently, the synergic effect between the conductive polymers and the semiconductor nanomaterials resulted in a significant improvement of the visible-light-driven photocatalytic activity of these hybrid nanostructured materials, which have been principally used for the degradation of hazardous chemicals as well as hydrogen production [277,279]. The main properties of the semiconducting polymers/metal oxide nanostructured photosensitive hybrid materials considered in this review are summarized in Table 6.

For example, a large portion of the conductive polymers-based hybrid photocatalysts has been prepared by using polyaniline (PANI), highly considered for its high conductivity, simple preparation, and reasonable stability [280,281]. PANI has been combined with many semiconductor metal oxides, such as TiO_2 [282,283], ZnO [284–286], ZrO_2 [287], CoFe_2O_4 [288], or SnO_2 [289] to prepare the composite photocatalysts developed to address the issue of water contamination by different mono- and multivalent heavy metal ions in recent years. A schematic illustration of the action mechanism of ZnO/PANI is represented in Figure 17.

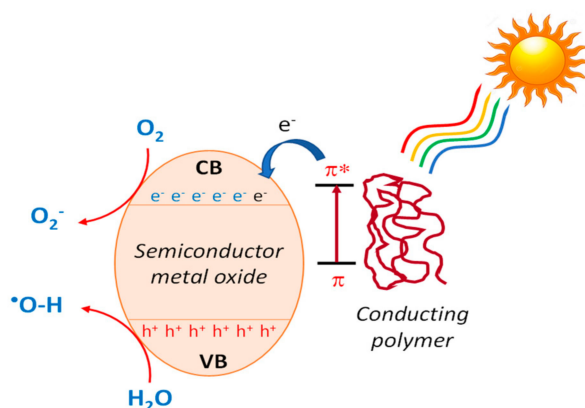


Figure 16. Schematic illustration of the mechanism of action of hybrid materials obtained by the combination of conductive polymers to semiconductor metal oxides.

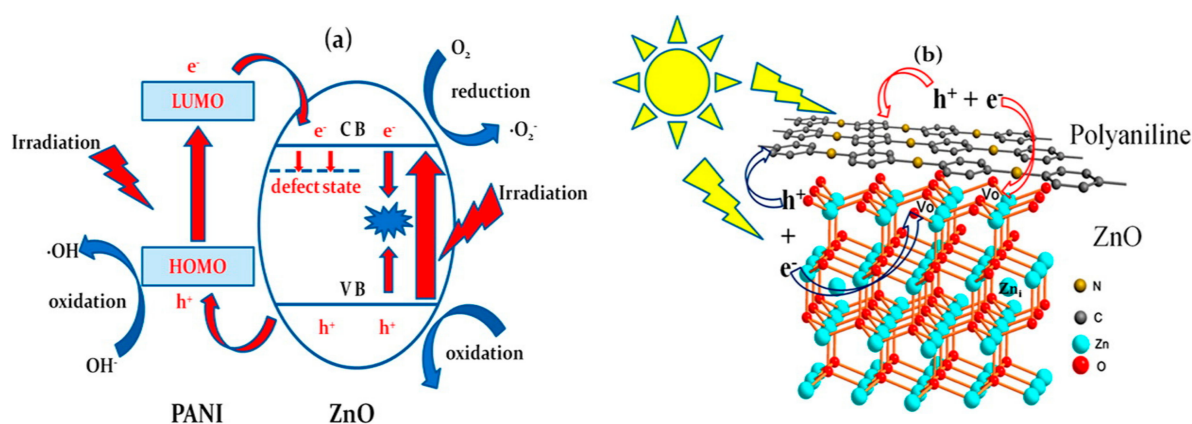


Figure 17. Proposed photocatalytic mechanism according to the band alignment (a). Atomic schematic diagram, illustrating the synergistic effect between defects and polyaniline (PANI) (b). Adapted and reprinted with permission from [285], Copyright (2014) American Chemical Society.

Another important conductive polymer is represented by polypyrrole (PPy), mostly used to produce nanohybrid photocatalysts for photodegradation of organic pollutants, and the photocatalytic performances of PPy-based materials have been affected by the fabrication method and type of irradiated light [277]. Many examples of hybrid nanomaterials with photocatalytic properties have been recently reported, in which PPy has been combined with different semiconductor metal oxides, such as TiO₂ [290,291], for pollutants degradation or hydrogen production, ZnO [292–294], and its derivatives doped with other metals, ZnWO₄ [295], Fe₂O₃ [296], or Fe₃O₄ [297–299].

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a poorly soluble polymer characterized by excellent electronic and optical properties, good optical transparency in its conducting state, high stability, and moderate bandgap, as well as a low redox potential [300]. Thanks to these properties, PEDOT has been reported to demonstrate high electrocatalytic activities for the oxygen reduction reaction [301], as well as an efficient catalyst in hydrogen generation and storage [302,303]. For this reason, PEDOT has been combined with many semiconducting metal oxides, such as TiO₂ [304], ZnO [305], or a combination of both metal oxides [306], determining an increase in the photocatalytic activity.

Similarly, polythiophene (PTh) has also attracted much great attention, as one of the most promising conducting polymers, able to significantly enhance the photocatalytic activity of the most common semiconducting inorganic photocatalysts. Indeed, PTh has been observed to be capable to increase the adsorption ability of the inorganic catalyst, also widening the light absorption region towards the visible light. However, only a few polythiophene (PTh)-based composite photocatalysts

have been actually reported and principally used for the photodegradation of organic pollutants and the CO₂ photoreduction [307].

Table 6. Main properties of semiconducting polymer/metal oxides hybrid nanomaterials and their photocatalytic activity data under visible irradiation or solar light irradiation. The best results achieved in each work are reported.

Semiconductor	Conductive Polymer	Preparation	Application	Productivity	Ref.
<i>n</i> -type TiO ₂ nanowells	PANI	In situ polymerization in ice-water bath	Photodetectors	Responsivity of 37 μ A/W–3.6 mA/W	[282]
3D-flowerlike TiO ₂ NPs	PANI	In situ oxidative polymerization	Congo red and methyl orange degradation (under UV and sunlight)	95% and 98% (UV); 90% and 96% (sunlight) after 2 h	[283]
Defective ZnO hybrids	PANI	Chemisorption method	Metyl Orange and 4-chlorophenol degradation (under UV light)	97% after 100 min 82% after 2 h	[285]
ZnO nanorods	PANI	Chemisorption method	Methylene blue degradation (under visible light)	98% after 60 min	[284]
ZrO ₂ nanoparticles	PANI	In situ chemical oxidative polymerization	Trichlorophenol degradation (under simulated sunlight)	~80% after 240 min	[287]
Hollow CoFe ₂ O ₄ nanofibers	PANI	Electrospinning, in-situ oxidative polymerization	Methyl orange degradation (under visible light)	85% after 120 min	[288]
SnO ₂ nanoparticles	PANI	In situ chemical polymerization	Cr(VI) reduction in aqueous medium (under visible light)	60%–100% after 210 min as function of concentration	[289]
TiO ₂ nanoparticles	PPy	In situ chemical polymerization	Diclofenac and 4-chlorophenol degradation (under simulated sunlight)	90% and 40% after 60 min	[290]
Pd/TiO ₂ nanoparticles	PPy	Simultaneous photodeposition method	H ₂ production (under UV-visible light)	1400 μ mol after 2 h (UV light); 3.5 μ mol after 2 h (visible light)	[291]
ZnO microrod arrays	PPy	Electropolymerization	Methylene blue degradation (under sunlight)	85.95% after 3 h	[292]
ZnO nanoparticles	PPy	In situ chemical polymerization	Diclofenac degradation (under simulated sunlight)	81% after 60 min	[294]
ZnWO ₄ nanoparticles	PPy	In situ chemical polymerization	Photoelectrodes	Tafel slopes of 76 and 84 mV dec ^{−1} for HER and OER	[295]
Fe ₂ O ₃ nanostructures	PPy	Hydrothermal method	Gas sensing	0.1–10 ppm of NO ₂	[296]
NiS/core-shell Fe ₃ O ₄ nanoparticles	PPy	In situ chemical oxidative polymerization	Cephalexin degradation (under sunlight)	80% after 30 min	[297]
NiS ₂ /NiO/core-shell Fe ₃ O ₄ nanoparticles	PPy	In situ chemical oxidative polymerization	Naproxen degradation (under visible light)	87% after 30 min	[299]
TiO ₂ nanotubes	PEDOT	Electrochemical polymerization and spin-coating	Photoelectrodes	12.9–20 mA/cm ² of photocurrent density	[304]
CNTs/ZnO nanotubes	PEDOT	In situ oxidative polymerization	Methyl orange degradation (under visible light)	75% after 200 min	[305]
TiO ₂ /ZnO nanostructures	PEDOT	In situ chemical polymerization	Hybrid nanodevices	52 S cm ^{−1} of electrical conductivity; 0.83 cm ² V ^{−1} S ^{−1} of charge carrier mobility	[306]

Definitely, the incorporation of conductive polymers has been demonstrated to significantly improve the visible-light-driven photocatalytic activity of hybrid nanostructured materials, by enhancing the separation of photogenerated charge carriers and extending the light absorption range. Based on these significant advantages, many nanostructured hybrids composed by semiconductor oxides conjugated with conductive polymers in different heterostructures have been designed, showing a promising photocatalytic activity, principally for water purification. Very high efficiencies in the degradation of organic molecules have been observed, with productivity values >80%–90%, and, in many cases, of a complete degradation within 1 or 2 h. Furthermore, the principal advantages for the use of photoactive polymeric-based materials are easy removal and long life, and control of the formation of secondary contamination is avoided. However, further steps appear necessary to better understand the mechanisms of action of these materials and their physicochemical features, with the aim to better improve the photoactivity, principally against the more insidious organic pollutants, as well as to extend their application field.

7. Hybrid Perovskites

Organo-inorganic hybrid perovskites have been largely explored to carry out semiconductor-based photocatalytic processes. In these compounds, the inorganic component is identified by the general formula ABX_3 , where A and B are transition metal cations, and X is a non-metallic anion, usually a halogen/oxygen anion. Actually, they hold great potential to harness solar light efficiently due to their peculiar photoelectronic properties, including strong light absorption, low exciton binding, as well as long photo-excited charges lifetime and migration. Moreover, the composition of both inorganic (A, B, and O) and organic components can be adjusted to tune bandgap and optimize photocatalytic efficiency towards the desired reaction [308–310]. Particularly, Pb-based organohalide perovskites, such as methylammonium lead iodide ($MAPbI_3$, MA = methylammonium), exhibit excellent photocatalytic properties due to marked light absorption, fast charge carrier migration properties, and poor recombination phenomena [309,311,312]. These systems have been deeply investigated in the last years as light-absorbing layers in perovskite-based solar cells, an emerging photovoltaic technology, which rapidly achieved record efficiencies, and showed promising performances in the fields of hydrogen production and organic synthesis (Figure 18) [312].

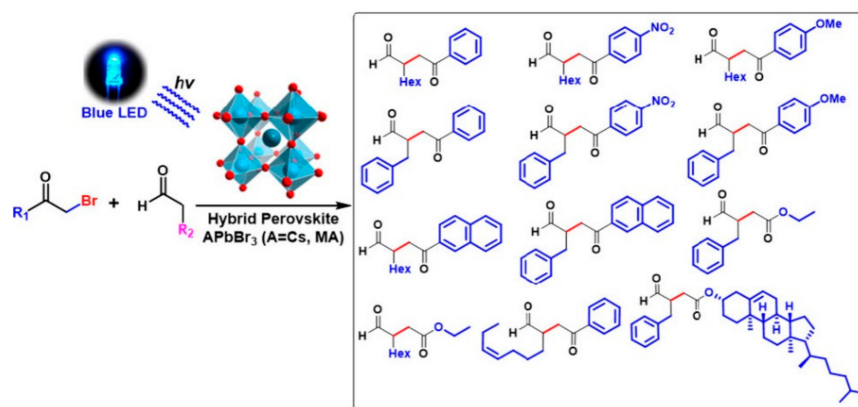


Figure 18. Scheme of α -alkylations reactions catalyzed by hybrid $MAPbI_3$, perovskites. Reprinted with permission from [312], Copyright (2019) American Chemical Society.

Nevertheless, their low-stability in an aqueous environment and lead-induced high toxicity strongly limit their applications [311,313]. Several strategies have been proposed to improve the stability of these systems. Notably, hybrid mixed halide perovskites— $MAPb(I_{1-x}Br_x)_3$ [314] and $MAPbBr_{3-x}I_x$ [315]—prepared by one-pot crystallization or post-synthesis ion exchange in a mixed halide solution, combine enhanced stability with improved photocatalytic activity for H_2 evolution in aqueous HX solution ($X = I, Br$), under visible light ($\lambda \geq 420$ nm). Alternatively, stable photocatalytic

hydrogen iodide (HI) splitting to H_2 can be achieved, exploiting the dynamic equilibrium of the dissolution and precipitation of $MAPbI_3$ [316]. Isolating $MAPbX_3$ perovskites from solvent molecules can be an effective method to improve their stability.

To this purpose, bulky capping ligands, such as aniline, can be bound to the surface of $MAPbBr_3$ system, exposing outwards hydrophobic phenyl groups, and, due to steric hindrance, protect the perovskite from corrosion, enhancing its stability [308]. Similarly, large conjugated organic cations can be employed as templating agents to produce stable lead halides, with narrow band gaps (2.01–2.35 eV) and, consequently, excellent photocatalytic activity and photochemical stability [317]. Also, the photocatalytic activity can be further improved by doping with additional co-catalysts [310]. In this way, composites of $MAPbI_3$ with reduced graphene oxide (rGO) [318,319], TiO_2 [320,321], or Ni_3C [322] are able to promote charge carrier transfer and separation and ensure a huge number of reactive centers on the surface. These features boost the efficiency of photocatalytic processes; actually, $Ni_3C/MAPbI_3$ composites disclosed hydrogen evolution rate as high as $2362 \mu mol g^{-1} h^{-1}$, about 55-fold higher than that of bare $MAPbI_3$ ($43 \mu mol g^{-1} h^{-1}$) and even higher than that of $Pt/MAPbI_3$ ($534 \mu mol g^{-1} h^{-1}$) (Figure 19). Table 7 reports a summary of the most promising hybrid perovskites and their photocatalytic features, as considered in this review.

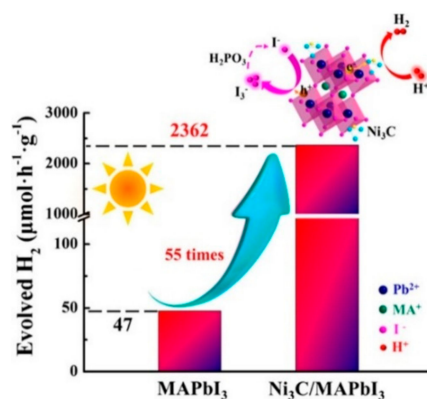


Figure 19. Comparison of H_2 evolution in aqueous HI solutions containing $MAPbI_3$ and Ni_3C decorated $MAPbI_3$. Reprinted with permission from [322], Copyright (2019) American Chemical Society.

In order to address toxicity issues, environmentally-friendly lead-free perovskites have been designed [309,311,323]. Among those, bismuthate perovskite, $(CH_3NH_3)_3Bi_2I_9$, have been rising great interest due to excellent stability in reaction environment, as well as a marked photocatalytic activity under visible light towards H_2 production [309] and water contaminants degradation (Figure 20) [323].

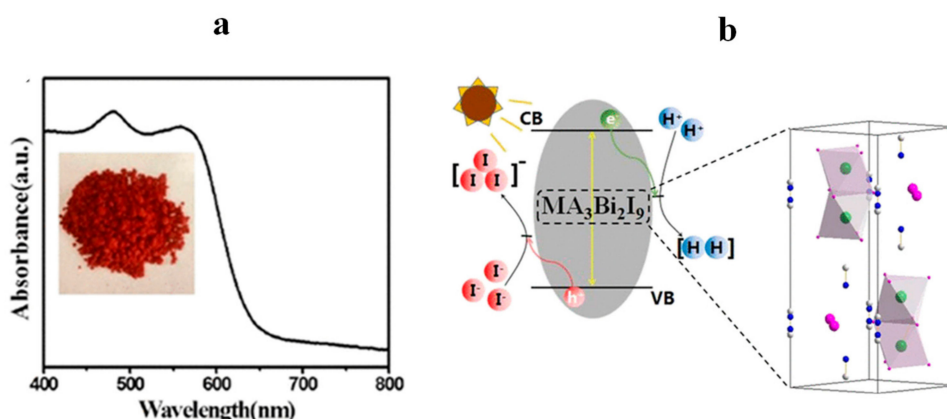


Figure 20. UV-Vis spectra (a) and schematic representation (b) of the $MA_3Bi_2I_9$ powder for H_2 evolution. Reprinted with permission from [309], Copyright (2019) American Chemical Society.

Finally, hybrid perovskites have been produced by different synthetic approaches and have shown outstanding photocatalytic performances, principally for H₂ production (in the range between 10–7000 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). Also, some environmental tests have been realized using hybrid perovskites to photodegrade the most common organic molecules, showing productivity values comparable with those obtained by the previously described hybrid nanomaterials.

Table 7. Hybrid perovskites and data on their photocatalytic activity under visible irradiation or solar light irradiation. The best results achieved in each work are reported.

System/Sample	Preparation	Application	Productivity	Ref.
Aniline-capped MAPbBr ₃ (MA = methylammonium ion, CH ₃ NH ₃ ⁺)	One-pot crystallization	Malachite green (MaG) degradation	90% in 70 min	[308]
APbBr ₃ (A = Cs or methylammonium)	One-pot crystallization	α -alkylation of aldehydes	99%	[312]
MAPb(I _{1-x} Br _x) ₃	One-pot crystallization	H ₂ production (HI splitting)	1471 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ for 62 cycles, 4 h each run	[314]
MAPbBr _{3-x} I _x	Light-assisted halide-exchange method	H ₂ production (HI splitting)	1021 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$; with Pt (co-catalyst) 2604 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$; For 6 cycles, 5 h each	[315]
MAPbBr ₃	Hydrothermal	H ₂ production (HI splitting)	34.4 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$; with Pt (co-catalyst) 60 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[316]
H[(Me) ₃ -TIB] ₂ Pb ₅ I ₁₇ (TIB = 1,3,5-tris(1-imidazolyl)benzene)	Solvothermal	MO, RhB, and MB degradation	100% in 60 min (MO, RhB) or 30 min (MB)	[317]
GO/MAPbBr ₃	Precipitation	CO ₂ reduction to CO	1.05 $\mu\text{mol cm}^{-2} \text{h}^{-1}$	[318]
rGO/MAPbI ₃	Hydrothermal	H ₂ production (HI splitting)	14 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ for 200 cycles (10 h each cycle)	[319]
Pt/TiO ₂ nanoparticles - MAPbI ₃	Hydrothermal	H ₂ production (HI splitting)	7277 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[320]
MAPbI ₃ -TiO ₂ nanorod array (TNAs)	Spin coating + heating at 70 °C	H ₂ production (HI splitting)	33.3 $\mu\text{mol cm}^{-2} \text{h}^{-1}$	[321]
Ni ₃ C/MAPbI ₃	Solvothermal	H ₂ production (HI splitting)	2362 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[322]
2-(aminomethyl pyridine)SbI ₅	Sol-Gel	H ₂ production	106.7 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ with GO (co-catalyst) 185.8 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[311]
(CH ₃ NH ₃) ₃ Bi ₂ I ₉	Hydrothermal	H ₂ production in HI aqueous solution	12.19 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ with Pt 169.21 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$	[309]
(CH ₃ NH ₃) ₃ Bi ₂ I ₉	Precipitation	RhB, MB	MB 70%; RB 100% in 130 min	[323]

8. Bioinspired Z-Scheme Photocatalysts

Recently, another feasible strategy for enhancing photocatalytic performance is spreading through the building of the direct Z-scheme photocatalysts, which are conceived based on biomimetic artificial photosynthesis [324,325]. Indeed, these materials owe their name to the fact that their charge transfer mechanism is similar to natural photosynthesis in green plants, in which the charge-carrier transport pathway involves a two-step photoexcitation that looks like the English letter “Z” (Figure 21a). Since 2013, when the concept of a direct Z-scheme photocatalyst was proposed for explaining the high photocatalytic formaldehyde (HCHO) degradation performance of the TiO₂/g-C₃N₄ composite [326], huge activities aimed to design and develop photocatalysts based on the direct Z-scheme have been conducted by several research groups.

The reactions in the natural photosynthesis are driven by the photogenerated electrons (in the CB of PS I), which can maintain a high reducing ability, and the photogenerated holes (in the VB of PS II), which can sustain a high oxidizing ability. Bio-inspired by the natural mechanism, an artificial Z-scheme photocatalyst has huge potential in achieving high photocatalytic performance. Specifically, the structure of a direct Z-scheme photocatalyst (Figure 21b) is similar to that of a type

II heterojunction photocatalyst, but its charge carrier migration mechanism is different. An artificial Z-scheme photocatalyst consists of two linked semiconductor photocatalysts. The former is an oxidation photocatalyst, which possesses a low VB position and exhibits a strong oxidation ability; the latter is a reduction photocatalyst, which usually has a high CB position, displaying strong reduction ability. Thanks to the peculiar charge transfer, a Z-scheme photocatalyst with excellent photocatalytic activity possesses several advantages: (i) simultaneous conservation of strong reduction and oxidation capabilities; (ii) spatial separation of reductive and oxidative active sites; (iii) high separation efficiency of photogenerated charge carriers with strong redox power; (iv) extended light-harvesting range, and (v) a wide spectrum of photocatalysts for specific photocatalytic reactions, indicating that coupling two photocatalysts with narrower band gaps meets the requirement of higher redox ability for these reactions [325,327].

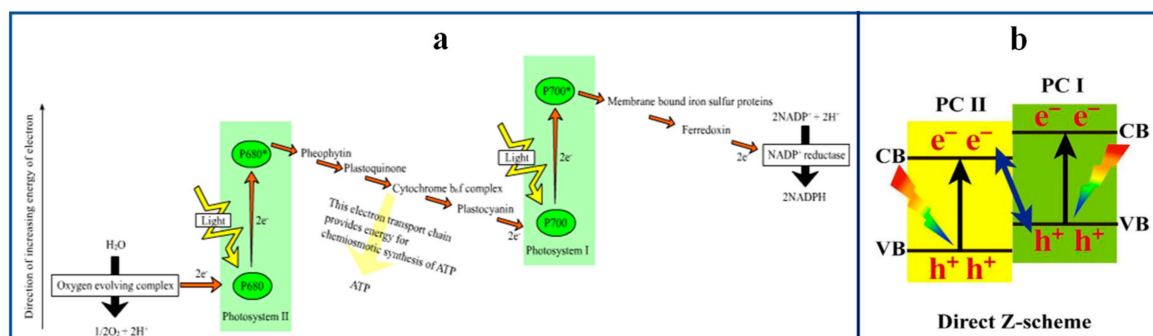


Figure 21. Panel (a) The mechanism of natural photosynthesis, in which P680 indicates the pigment (chlorophyll) that can absorb 680 nm light in photosystem II (PS II), and P680* is the excited state of P680. P700 indicates the pigment (chlorophyll) that can absorb 700 nm light in photosystem I (PS I), while P700* is the excited state of P700 (Z-scheme. Available online: <http://commons.wikimedia.org/wiki/File:Z-scheme.png>, accessed on 9 January 2020). Panel (b) Schematic illustration of direct Z-scheme heterojunction, in which CB, VB, PCI, and PCII indicate the conduction band, valence band, photocatalyst I, and photocatalyst II, respectively. Reprinted with permission [325]. Copyright Elsevier 2018.

Nanostructured hybrid materials, combining inorganic and organic components at the molecular scale, allow intimate interaction at the interface, as well as fine tuning of photoelectronic properties required to achieve ideal bandgap matching; thus, they are ideal candidates to build Z-scheme photocatalysts. Actually, most of the previously described systems can be efficiently combined into a nanocomposite featuring direct Z-scheme heterojunction. Notably, some of them, such as carbon-based materials (graphene oxide, reduced graphene oxide, and especially graphitic carbon nitride) and MOFs, can act as electron mediators required in a solid-state Z-scheme mechanism [219,328–331].

Z-scheme photocatalysts are, therefore, intensively studied in the last few years and are promising in various applications; the latter include water splitting, carbon dioxide reduction, degradation of pollutants, and biohazard disinfection. The selection of suitable semiconductors with appropriate band structures is a prerequisite for the successful fabrication of direct Z-scheme photocatalyst. However, although they have been widely investigated until now, the obtained photocatalytic efficiency is still moderate and far from the requirement for practical applications. Many studies are still needed to achieve the real application of artificial photosynthesis.

9. Conclusions

The fields of semiconductor-based solar light harvesting for photocatalytic and related applications are rapidly evolving in various directions. The combination of inorganic semiconductors with organic photoactive compounds, polymers, or C-based materials is showing great potential, inducing emerging properties in the resulting hybrid heterostructures, depending on the physicochemical and electronic interaction between the components. Among the advantages offered by hybrid materials, extended

light absorption and improved charge separation efficiency and lifetime are frequently obtained, along with the possibility to match the conduction and valence band positions, achieving suitable redox potential for specific reactions. Currently, TiO_2 remains the reference photocatalyst, followed by ZnO ; however, other semiconductors are revealing promising photochemical properties, which deserve further insight and could be improved through the mentioned approaches.

Dye sensitization is a well-established strategy, offering a huge variety of molecular structures and optoelectronic properties. Much research is focused on seeking effective metal-free dyes, possibly inexpensive or deriving from natural sources. Ligand-to-metal charge transfer sensitization seems promising but relatively less developed and opens the way to progress. Its main advantage is the possibility to use small molecules that are cheaper and easier to synthesize than large dye compounds. The stability and reusability are crucial points for this kind of sensitized photocatalysts and can be faced by carefully choosing the synthesis route and conditions and the ligand structure, in order to obtain stable binding of the sensitizers, possibly through covalent bonds and/or multiple anchoring groups.

Graphene, reduced graphene oxide, C nanotubes, C quantum dots, graphitic C_3N_4 , and other carbon materials provide huge advantages in conjugation with metal-based semiconductors, allowing to design a wide variety of hybrid nanocomposites with tunable properties. They can act as sensitizers and/or electron acceptors, reducing recombination and enhancing electron transport and light conversion efficiency. TiO_2 , ZnO , Cu_xO , and Fe oxides are widely explored in this scope. Conductive polymers offer similar benefits and may turn useful in the preparation of stable and recyclable photocatalysts, additionally serving as supports for oxide nanostructures.

In the last years, metal-organic frameworks (MOFs) are emerging as multifunctional materials, with several combinations of metals and linkers offering tailored structures and properties. Many examples of MOFs with outstanding photocatalytic performances are already available, but their potential is still to be fully exploited. Hybrid perovskites, intensely studied in solar cells, are also attracting interest for their radiation harnessing ability.

As regards the applications of hybrid photocatalysts, the removal of water pollutants is widely investigated, though the most used substrates are still dyes and simple model organic molecules, while there are limited focalized studies on the degradation mechanisms of more complex contaminant compounds of emerging concern. An impressive number of works deal with hydrogen generation through water splitting, one of the main future challenges, in which further advances are expected. The production of solar fuels through CO_2 reduction is also receiving growing attention but needs strong improvements. On the other hand, an attractive field that seems to have still much to disclose is organic synthesis. Apart from photocatalytic selective oxidations, few organic conversion reactions have been explored in detail on hybrid photocatalytic systems. Limited data are available also on the light-induced antimicrobial activity of hybrid photosensitive materials, which is an application with a strong practical interest. Moreover, the feasibility of the scale-up from the laboratory to a chemical plant scale, which is a fundamental step toward the practical application, is rarely considered.

10. Perspectives

The sunlight harvesting represents an ambitious objective of ongoing research efforts. Hybrid organic-inorganic sunlight-capturing nanomaterials will attract a great deal of attention due to their unique ability to manipulate light and control energy flow at nearly the atomic level. However, there are still many challenges need to be addressed before they are fully used in practical applications with high commercialization. Indeed, to make solar energy economically competitive with other energy sources, it is critical to find ways to reduce the costs and, at the same time, to improve efficiency and performances. A huge variety of novel photocatalytic materials is being proposed; however, a detailed assessment of their electronic and physicochemical properties and their functional behavior is necessary. Particular attention should be devoted to the stability of the photocatalysts in the reaction environment, which is often a limitation to their long-term activity and recycling efficiency, and the reproducibility of both synthetic procedure and catalytic performances.

For this reason, it can be expected that the current knowledge on the various classes of photoactive systems will inspire the researchers' creativity for the design and development of novel hybrid materials, even by the combination of some of the presented systems, and relying on less known promising semiconductors. The aim will be the optimization of tailored materials for the utilization of solar radiation energy in specific processes in energetic, environmental, and industrial fields, eventually making these photocatalytic processes competitive with traditional technologies. Furthermore, many types of hybrid systems attract interest also in other fields, which request nanomaterials, showing a very broad photo-response or a specific sensitivity to some radiation ranges, e.g., photovoltaic cells and photodynamic therapy. The flexible and tunable optical and electrochemical properties offered by dyes, MOFs, carbon materials, conductive polymers, and their combinations may turn increasingly useful for these applications as well.

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