Selected hybrid photocatalytic materials for the removal of drugs from water

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The interest toward the development of hybrid photocatalytic materials is exponentially grown in the last decade. In this review, we summarize the current research progresses in the production of hybrid materials, with a particular focus on carbon based material coupled with titanium dioxide, photo-biocatalysts, and their application in the removal of emerging contaminants from water, i.e. pharmaceutical products. We give some highlights on the key properties and features of these advanced composites, the involved mechanisms and on the potential hazards posed by these nanomaterials.

Keywords
Photocatalysis, Hybrids materials, Photobiocatalysts, Toxicity, Drugs removal, Carbon-based materials.

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Introduction

Since the discovery of the heterogeneous photocatalysis the scientists focused their attention on innovative strategies for increasing the overall process efficiency.

The most prominent drawback of the photocatalytic process is the scarce efficiency, due to the imbalance between the low kinetic of separation and transfer of the photogenerated charge carriers (hole in the valence band, h_{vb}^+, and electron in the conduction band, e_{cb}^-) and the high kinetic of recombination in the bulk of the semiconductor and/or mediated by surface species or adsorbed molecules [1]. Unfortunately, for the main stable and photoactive semiconductors, the scarce efficiency is not compensated by high Visible absorption, as the main semiconductors used in photocatalysis (TiO_2, WO_3, $ZnO...$) absorb the UV fraction of the solar spectrum only.

The synthesis of hybrid structures coupling semiconductors with one or more organic/inorganic phases have been proposed not only to increase the overall efficiency of the process, but also to visible-sensitized the process itself [2–4].

With the term *hybrid material* we usually denote a material formed by coupling two or more phases (inorganic or carbon based) with features that are not the sum of the properties of the single phases, but the result of the synergistic interaction among them. The hybrid shows properties specifically related to the close interaction among the phases and to the peculiar features of the interface properties.

In the last 10 years, the attention has been strongly focused on the new possibilities that the photocatalytic hybrid materials give to overcome the main drawbacks of the photocatalytic process based on traditional materials (see Figure 1 and its inset). It is manifest that the studies on hybrid structures have reached a prominent role in the field of photocatalysis, e.g. in the first months of 2017 more than 50% of the publications related to photocatalysis is directly or indirectly connected to hybrid materials. Restricting the analysis to the use of hybrid materials for the photo-assisted abatement of pollutants (and limiting the analysis to the period from 2015 to present) it emerges that in more than 75% of the articles in which the photocatalytic activity of an hybrid materials has been tested, this evaluation was carried out by using a single dye as standard substrate. Of the remaining 25%, only a minimal fraction (2–3%) is focused on the abatement of pharmaceutical products.

The main advantages of hybrid materials for photocatalytic applications are the following: 1) the presence of a gradient of potential at the interface can in some cases assist the separation of the photogenerated charges in the proximity of the interface; 2) one of the phases is usually able to absorb visible light; 3) some of the most promising hybrid photocatalysts have high adsorption properties due to their high surface area; 4) the coupling of a second phase with a traditional semiconductor can promote an increment of the selectivity of the process.

On the basis of the most general definition for hybrid materials the principal types of hybrids proposed for photocatalytic applications are:

1) homo- or hetero-materials composed by two or more inorganic phases [5–7];

Figure 1
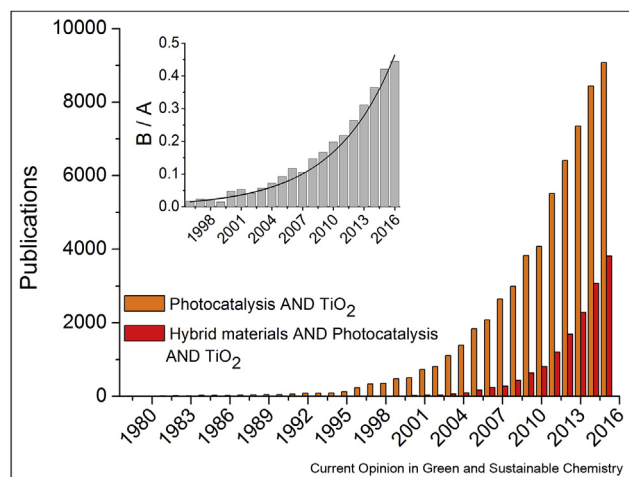
Number of publications from 1978 to 2015 indexed with the key words *Photocatalysis* and *TiO₂* (A) and with *Hybrid materials* and *Photocatalysis* and *TiO₂* (B). Insert: ratio B/A as a function of the publication years. Source: Scopus, March 2017.

2) inorganic semiconductors coupled with carbon-based materials (CBMs) such as graphene (GR) [8−10], graphene oxide (GO) [11,12], reduced graphene oxide (rGO) [13−15], single or multiwalls carbon nanotubes (CNTs) [16−18], carbon quantum dots [19], carbon nano-horns [20] and fullerenes [21,22];

3) inorganic semiconductors hybridized with innovative 2D materials such as graphitic-carbon nitride (g-C_3N_4) [23−25] or boron nitride (BN) [26];

4) photocatalysts composed by inorganic semiconductor/polymer nano-hybrids [2];

5) inorganic semiconductors surface-functionalized with species able to visible-sensitizing the photocatalyst [27], increase the photocatalytic process selectivity (e.g. TiO_2/enzymes [28]) or increment the adsorption of the materials toward selected classes of molecules [29].

Focusing on the class of hybrids coupling TiO_2 and graphene (or graphene-like structures), it is possible to divide the materials in two classes (here defined as A and B). Class A includes all the materials in which the semiconductor is synthesized in situ on graphene (e.g. graphene nanoplatelets, eventually functionalized with −COOH or −NH₂ moieties, can be used as nucleation sites for TiO_2 particles), while Class B contains the hybrids in which graphene is typically synthesized on pre-existing semiconductor particles by reduction of adsorbed GO (e.g. by thermal annealing, photocatalytically, chemically with hydrazine…).

In the light of the impressive number of studies regarding the photocatalytic properties of hybrid systems, this short review is focused on a restricted subgroup of materials. The attention is devoted to TiO_2-based hybrids avoiding the analysis of alternative inorganic semiconductor-based materials which usually have lower efficiency than TiO_2-based hybrids. Furthermore, we did not consider the fully inorganic hybrid systems focusing the attention on the organic/inorganic materials only. Finally, we restricted our analysis to the use of these for the abatement of organic bio-recalcitrant pollutants reporting some case studies about drugs removal, excluding the impressive amount of articles focused on the decoloration of dyes because the too widespread practice of testing the photocatalytic materials toward a dye only creates problems of interpretation. It is true that the organic dyes are among the largest group of pollutants discharges from the industries, but their operational transformation mechanism under irradiated hybrid systems (primarily a visible sensitized photo-bleaching promoted by the injection of electrons from dye excited states towards delocalized and empty states of the hybrid) can be quite different with respect to a pure photocatalytic process. Consequently, as recently demonstrated in Ref. [30], this approach cannot give informative indications about the real photocatalytic efficiency of the material.

TiO₂/CBM hybrid materials applied to drugs removal

Different processes occur during the photo-activated degradation of a pollutant in the presence of nano-photocatalysts coupling TiO_2 and a narrower band gap CBM. CBM is easily excited under visible light despite of TiO_2 that requests hν ≤ 360 nm. Electrons and holes generated (in CMB and/or TiO_2 as a function of the irradiation) can migrate through the interface and react at the surface and/or recombine (in the bulk, at the interface or at the surface). The direction of transfer of the photogenerated charges as well as the place in which the transformation of the pollutant mainly occurs cannot be easily generalized and primarily depends on the band-edge energy position, the charge carriers mobility and the features of the TiO_2/CBM interface. A complete agreement on the role of the carbonaceous phase during the photocatalytic process has not been reached. Different mechanisms can be operational as a function of the specific properties of the hybrid systems. The carbonaceous phase (i.e. rGO) can operate in three different ways: 1) rGO acts as a good electron acceptor and promotes the electron transfer from TiO_2 to rGO ($e^-_{CB(TiO_2)} \rightarrow$ rGO) as a consequence of the relatively high work function of graphene (4.42 eV) [31], furthermore $h^+_{VB(TiO_2)}$ can move toward rGO promoting the oxidation of here adsorbed substrates; 2) rGO absorbs visible (and UV photons) promoting the delocalization of electrons located in high-energy rGO states onto TiO_2 (rGO $\rightarrow e^-_{CB(TiO_2)}$), acting more as a macromolecular sensitizing instead of electron reservoir [32]; 3) the rGO

has a detrimental effect on the overall photocatalytic efficiency as a consequence of either the absence of electron/hole transfer between TiO_2 and rGO and vice-versa (rGO is a competitive light absorber and can often compartmentalize the substrate on a non-reactive phase) or the ability of rGO to capture both holes and electrons generated into TiO_2, acting as a macromolecular recombination center. For a more detailed description of the possible reactive schemes please refer to [15].

The degradation rate of standard pollutants is usually used to compare the efficiency of different materials, taking into account that many experimental parameters affect the process, including the concentration and kind of molecules, the amount of photocatalyst, the type and intensity of irradiation.

The absence of papers related to TiO_2-non defective graphene nanoplatelets (GNP) used toward drugs abatement has to be ascribed to the difficulty to couple the two phases with opposite solvophilic properties: the hydrophobic GNP and the hydrophilic TiO_2. The absence of helpful interfacial phenomena implies that GNP only acts as competitive light absorber. Conversely, the amphiphilic nature of GO/rGO surface allows the occurrence of a strong interaction between the organic and inorganic phases with the establishment of the series of reactions/mechanisms briefly described above.

TiO_2-rGO materials, synthetized through different approaches, were successful applied to the degradation of acetaminophen [33], diphenhydramine [34,35], carbamazepine [36–39], atenolol [40], diclofenac [41], ibuprofen [38], sulfamethoxazole [38] and risperidone [42]. There is an overall agreement about the possibility to obtain a positive role of GO/rGO on the analyte degradation rate and about the requirement of low carbon loadings, due to the shielding effect on light, while it is under scrutiny if GO/rGO phase could act as sensitizer toward visible light [15,42].

TiO_2-CNT composite materials exhibit controversial efficiency. TiO_2-single wall CNTs were tested on the degradation of a mixture of 22 pharmaceuticals [43], showing that the performance of composite materials is strongly dependent on the kind of molecule. TiO_2-multiwalls CNT under UV irradiation could have a positive effect (ketoprofen [44] and bisphenol A [45]), negative effect (salicylic acid [46] and diclofenac [45,47]) or controversial (carbamazepine [48,49]), but data are not enough to conclude if this phenomenon is linked to the kind of molecule, CNT diameter or the presence of oxidized moieties on the CNT structure.

Other and less common carbonaceous phases were used into TiO_2 composite in the drugs removal, such as fullerenes [50,51], carbon dots [52] and organic shell layer [53].

TiO_2- and CNP-based photobiocatalysts

A photobiocatalyst is a semiconductor with or without a light harvester that activates an enzyme. Usually, it is a four component system, comprising a photocatalyst, an enzyme and two chemical compounds acting as sacrificial electron donor (e.g. water, alcohol or tertiary amines) and an electron relay between photocatalyst and enzyme. Different systems could be prepared, all inspired to natural photosynthesis [28].

A great interest is associated to the development of photocarbocatalysts [54–56] that could be employed to promote enzymatic reductions mediated by NAD^+/NADH. GO and CNTs form strong association complexes with many aromatic organic molecules and can promote the assembly of organic chromophores to introduce light-harvester centers on the carbon.

Another promising application is to exploit the H_2O_2 produced by a semiconductor (i.e. TiO_2) to activate enzymes, as depicted in Figure 2. Virtually all photocatalytic systems in the presence of oxygen generate ROS as a consequence of the efficient trapping of conduction band electrons by oxygen. The primary species is superoxide $O_2^{\bullet-}$, easily protonated by water to form $\bullet OOH$ that can end up in H_2O_2 by a second electron and

Figure 2
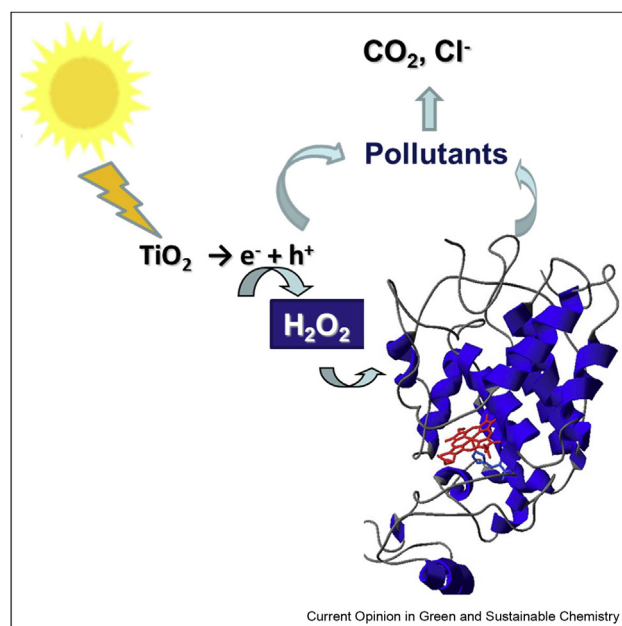
Mechanism describing the possibility to exploit the photocatalytic production of H_2O_2 under an irradiated semiconductor (i.e. TiO_2) to activate enzymes.

a protonation step. Even if the generated stationary concentration of H_2O_2 is generally low, it should be sufficiently high and compatible with enzyme activation as most of the peroxidase and catalase enzymes can operate with low H_2O_2 concentration. This approach was successfully applied to the degradation of chlorophenols and carbamazepine combining peroxidase and TiO_2 [57,58]. TiO_2 and peroxidase act synergistically, leading to an increase in the removal rate of model molecules. Furthermore, this system exhibits a certain selectivity on the intermediates products, i.e. in the case of dichloro and trichlorophenols the formation of chloroderivatives is hindered [57]. As for carbamazepine, photocatalytic treatment prevails on the enzymatic degradation, but the synergistic effect of two catalysts leads to a more efficient carbamazepine degradation [58].

Toxicity related to TiO_2, CBM and composite materials

The toxicity of photoactive nanomaterials depends on the intrinsic physicochemical properties of the primary particle (particle size, morphology, crystal structure, surface area, band gap energy, and charge), nanoparticle behaviors in the environmental media (aggregation, agglomeration, and sedimentation) and on the organism surface [59]. Owing to their unique physicochemical properties, the risk assessment is complex and challenging and current available data, collected in Table 1, are inadequate to draw conclusions about their potential hazard.

However, numerous materials cause oxidative stress, such as Graphene, CNTs, and TiO_2; for TiO_2 a phototoxic effect was shown toward numerous organisms and cell lines [60,61]. Toxicity is depended on nanoparticles concentration as well as irradiation intensity and duration; particle size plays a key role as well and the highest phototoxicity toward *Daphnia magna* was exerted by intermediate sized particles [61].

Concerning CBM, studies are controversial and range from considering graphene materials as biocompatible to pose adverse biological responses and cytotoxicity [62]. Though, the available data suggest that placenta does not constitute an impermeable barrier for the nanomaterials and they possess a potential toxicity; oxidized graphene forms seem less toxic than graphene sheets or multiwall carbon CNTs [63]. Furthermore, graphene poses toxic effects on different biological models, while GO exhibits a low cytotoxicity [64].

Few toxicity studies are available on composite materials. TiO_2-GO composites exhibit significant cytotoxicity with a decrease of cell viability as well as TiO_2, while GO could enter A549 cells without causing any cell damage [65]. The cytotoxicity of composite material has been attributed to oxidative stress related to TiO_2 nanoparticles. As a confirm, TiO_2-GO composite was separated into TiO_2 and GO after entering into A549 cells, so assessing that the composite material exerts the combined toxicity of the two separate materials, without any additional effect. Similar conclusions arose from tests performed using *Daphnia magna* and *Oryzias latipes* on TiO_2 and graphene–TiO_2 nanocomposite as the combined system does not exhibit a higher toxicity [66].

Table 1

Toxicity performed on TiO_2, carbon-based materials and composite materials.

Toxicity test	Materials					
	TiO_2	CNT	GNP/rGO	GO	TiO_2/GNP	TiO_2/GO
Cytotoxicity	Significant cytotoxicity [65]	Oxidative stress [67]	More toxic than GO [68]	No cell damage [65,69]	–	Significant cytotoxicity [65]
Daphnia magna	LC_{50} 118 ppm (dark), 60 ppm (SSR) [66]; EC_{50} 1.1 (25 nm) [69]	–	–	–	LC_{50} 138 ppm (dark), 90 ppm (SSR) [66]	–
Oryzias latipes	LC_{50} > 500 ppm (dark), 8.5 ppm (SSR) [66]	–	–	–	LC_{50} > 500 ppm (dark), 11 ppm (SSR) [66]	–
Zebrafish	–	Death [63] reduced heart rate [70]	Reduced larva length [70]	Malformations [63] Reduced heart rate [70]	–	–
Hyalella Azteca	LC_{50} 24 ppm (low conc), 44 ppm high conc [71]	–	–	–	–	–
Animals	–	Increase embryonic death, decrease embryonic growth (Chicken [70])	Lung inflammation (mice, [62]); Decreased survival rate [71]	Controversial effect (mice [62])	–	–
Cells	–	Decrease cell viability [72]	Induced apoptosis (rat [62])	Oxidative stress (human lung [62])	–	–

Perspectives and conclusive remarks

Even if some of the proposed innovative hybrid materials showed quite interesting features, their overall photocatalytic performances are not so impressive to foresee a large use of these materials in the industry of photocatalytic materials in a near future. Furthermore, despite the enormous efforts spent, a real comprehension of the mechanism active on these materials under irradiation and their ability to remove classes of pollutants different from the dyes has not been reached yet. In our opinion, in the field of the photocatalytic hybrid materials it is essential: 1) to test the new systems with substrates that do not absorb visible light and of more environmental concern (e.g. pharmaceutical and drugs) and in conditions closer to real applications; 2) to design the photocatalytic experiments with the aim to clarify the operational mechanisms comparing the results obtained with different substrates and under different irradiation systems; 3) to evaluate the real possibility of a wide-scale application of the hybrid materials in term of cost of production, environmental-sustainability of the synthesis; as an example, the production of GO through the exfoliation of graphite oxide obtained by the Hummers' method (oxidation of graphite by strong oxidants in mineral acids) must be carefully evaluated from the point of view of the environmental implications, and 4) to analyze thoroughly the toxicity effects of both the materials itself and the by-products obtained from the photocatalytic transformation of the considered pollutants.

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