Review

Photocatalytic composites based on titania nanoparticles and carbon nanomaterials

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Abstract

In this article we present a review on recent experimental works toward the formation of visible light responsive composite photocatalysts on the basis of titania nanoparticles and carbon nanomaterials of different types. The research results achieved in last years has shown that the nanocomposite photocatalysts comprising titania nanoparticles and graphene or graphene oxide sheets, and also nanoparticles of noble metals and metallic oxides, exhibited the evident priority compared to the others. Therefore our review emphasizes the research on these promising visible light responsive nanoparticles photocatalysts.

Keywords: nanocomposite, photocatalyst, titania, carbon nanotubes, graphene

Classification numbers: 4.02, 5.07, 5.14, 5.15

1. Introduction

The application of advanced oxidation processes with the key role of stable oxide semiconductors such as TiO₂ is an efficient method to degrade toxic organics in water environment. On the basis of this method, pilot-plants for photodegradation and photomineralizations of phenol, dichloromethane and tetrachloroethylene in aqueous solution by titania immobilized on membrane were constructed since two decades ago [1, 2]. The photooxidation of prometryn and prometon in aqueous solution by hydrogen peroxide on photocatalytic membrane immobilizing TiO₂ [3] and photocatalytic degradation of pesticide pirimiphos-methyl (PMM) [4] were also studied at that time. The current state and developments of heterogeneous photocatalytic degradation of phenols in wastewater was presented in the review [5]. In the experimental work [6] the effectiveness of photocatalytic treatment using titania in the degradation of 44 organic pesticides was evaluated. The photocatalytic degradation of tetracycline in aqueous solution by titania nanoparticles (NPs) was investigated in reference [7]. An efficient improvement of photocatalytic process is to apply the photoelectrocatalytic oxidation: the electrons photogenerated at the TiO₂ anode are driven to a counter cathode via an external circuit. The photoelectrocatalytic process can prevent charge recombination and extends the life time of the active holes [8].

Beside the priorities of TiO₂ over other oxide semiconductors, for using in photocatalytic and photoelectrocatalytic degradation of toxic organics by sunlight irradiation it has following drawback: due to its large bandgap, titania can absorb only a small portion of sunlight energy. There are three different ways to overcome this drawback: (i) doping TiO₂ by a suitable cation or anion, (ii) using a hybrid nanostructure TiO₂ @Au or TiO₂@Ag comprising a TiO₂ nanoparticle (NP) and a noble metal Au or Ag one, and, (iii) using a nanocomposite comprising a TiO₂ nanostructure, mainly TiO₂ NP, and a carbon nanostructure such as carbon nanotube (CNT), fullerene (C₆₀), and graphene (G) or
graphene oxide (GO). Previously the experimental research on titania doping by different cations and anions has been reviewed (see reference [9], for example).

In TiO$_2$-Au nanostructures, Au nanoparticles may play various roles. In reference [10] it was shown that the photoexcited semiconductor NPs undergo charge equilibration when they are in contact with metal NPs. Such a charge redistribution induces the shift of the Fermi level in semiconductor NPs to a more negative potential. The transfer of electrons to gold NPs was probed by exciting semiconductor NPs and determining the apparent Fermi level of the hybrid system. The shift of Fermi level is size-dependent: 20 mV and 40 mV for gold NPs with diameter of 8 nm and 5 nm, respectively.

Plasmon-induced charge separation at TiO$_2$ films loaded with gold NPs was investigated in reference [11]. Photoaction spectra for both the open circuit potential and short-circuit current were in good agreement with the absorption spectrum of gold NPs in TiO$_2$ film. Thus gold NPs are photoexcited due to the plasmon resonance and charge separation is accomplished by the transfer of photoexcited electrons from gold NPs to TiO$_2$ conduction band and the simultaneous transfer of compensative electrons from a donor in the solution.

The charge separation and photocatalytic activity of Ag@TiO$_2$ core–shell nanostructure under UV-irradiation was investigated in reference [12]. Photoexcitation of TiO$_2$ shell results in accumulation of electrons in Ag core, as evidenced from the shift in the surface plasmon band from 460 to 420 nm. The stored electrons are discharged when an electron acceptor is introduced into the system. Charge equilibration with redox couple shows the ability of these core–shell nanostructures to carry out photocatalytic reduction reactions. The charge separation, charge storage and interfacial charge transfer steps following the excitation of the TiO$_2$ shell were discussed.

In reference [13] a plasmonic photocatalyst consisting of silver NPs embedded in TiO$_2$ was investigated. The excitation of localized plasmon polarizations on the surface of silver NPs causes a tremendous increase of the near-field amplitude at well determined wavelengths in the near-UV. The photocatalytic behavior of TiO$_2$ was greatly boosted due to this enhancement of near field amplitude.

In this work we focus on the review of research results concerning the improvement of the photocatalytic activity of different titania-nanocarbon composites in comparison with the photocatalysts comprising only titania NPs or carbon nanostructures, with the emphasis on graphene and graphene oxide.

Section 2 is a short review of several important works on the photocatalytic degradation of toxic organic pollutants on the composite photocatalysts comprising CNTs of different types and titania NPs. The main content of this review, section 3, is the detailed presentation on composite photocatalysts comprising titania NPs and graphene (G) or graphene oxide (GO). Since the results of a large number of research works on titania-graphene or graphene oxide have been included in a recent comprehensive review [14], we shall present only the contents of the articles published later than those included in reference [14]. The conclusion and discussions will be presented in section 4.

2. Photocatalytic nanocomposites comprising titania and carbon nanotubes of different types

The study of the photocatalytic degradation of toxic organic pollutants on titania-CNTs began a long time ago. Faria et al [15] have prepared multi-walled carbon nanotube (MWCNT)-titania composite photocatalysts by means of a modified acid-catalyzed sol-gel method from alkoxide precursors. The photodegradation experiments were carried out in a glass immersion photochemical reactor charged with 800 ml of aqueous solution/suspension. The solution/suspension was magnetically stirred. The irradiation was often performed in air with continuous stirring to supply enough oxygen for oxidation photodegradation. It was observed that phenol decomposition in the presence of MWCNT as well as the direct-photolysis without any solid is negligible with less than 5% conversion within 4 h UV irradiation. Complete disappearance of phenol (more than 95% of conversion) is observed in about 6 h of UV irradiation for neat TiO$_2$. The introduction of MWCNT into TiO$_2$ by a modified sol-gel method remarkably induces a kinetic synergetic effect in phenol disappearance. An optimum of the synergetic effect was achieved for MWCNT–TiO$_2$ composite with MWCNT/TiO$_2$ weight ratio equal to 20%. The increase of this ratio results in the increase of phenol conversion after 4 h of irradiation from 46.2 to 97.3%.

Gray et al [16] have investigated the efficiency of the reduction of charge recombination and the enhancement of photocatalytic activity by anatase TiO$_2$–CNTs composite nanostructures. These photocatalysts were prepared by means of a simple low-temperature process in which CNTs and titania NPs were dispersed in water, dehydrated at 80 °C and dried at 104 °C. Charge recombination was investigated by measuring photoluminescence spectra of selected composite. The photocatalytic activity of the prepared materials was studied by investigating the phenol degradation. Over the course of 60 min reaction time, no phenol loss was observed in the presence of either single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs) alone at a loading of 10 mg l$^{-1}$. Thus, under these reaction conditions the phenol adsorption to CNT surface and volatile loss were negligible. The phenol degradation rate by TiO$_2$–SWCNTs composite was attained at optimum SWCNT/TiO$_2$ weight ratio equal to 1:20. The corresponding degradation rate is 2.5 times higher than that of P25 powder and more than 4 times higher than that of anatase powder. Adding more SWCNTs did not increase the degradation rate, probably because a higher concentration of SWCNT bundles reduces the light intensity on the TiO$_2$ surface.

Following mechanism for the enhanced photocatalysis of SWCNT/TiO$_2$ composite was proposed: each anatase NP is in intimate contact with SWCNTs. Under UV irradiation the electrons are excited from valence band to conduction band of anatase, creating holes in valence band. In the absence of
SWCNTs most of these charges quickly recombine. When SWCNTs are attached to the surface of anatase, the relative position of SWCNT conduction band edge permits the transfer of electrons from anatase surface into SWCNT, allowing charge separation, stabilization, and hindering recombination. The longer life of holes in the valence band of anatase accounts for the higher photocatalytic activity. Although the MWCNT/TiO₂ composites behave similarly, they do not enhance the photocatalytic activity to the same extent as the SWCNT/TiO₂ composites do, because there is much less individual contacts between MWCNT and anatase surface.

A novel modified sol-gel method based on the surfactant wrapping technique was developed by Li Puma et al [17] to prepare a mesoporous nanocomposite film by coating a uniform nanometer-scale titania layer on individual MWCNTs. The study of photoelectrocatalytic activity of the prepared nanocomposite was carried out in a specially designed photoelectrochemical reactor. Methylene blue (MB) trihydrate was used as the model compound for the photo-oxidation experiments. The enhancement effects induced by the combination of CNT/TiO₂ composite, irradiation and electrical bias (i.e. electrode potential) were determined. Control experiments showed that composite, irradiation or potential alone have no effect on MB degradation. The reduction of MB in the first 60 min is common to each of the experiments and can be mostly attributed to physical adsorption of MB on the reactor wall. The tests with irradiation and potential on bare graphite electrode or composite and potential in the reactor wall. The tests with irradiation and potential on bare graphite electrode or composite and potential in the absence of irradiation were also found to have no effects.

The irradiation of the composite in the presence of a positive potential resulted in a significant increase of MB degradation rate. A clear enhancement of the degradation rate in the experiments with CNTs/TiO₂ composite was also observed when compared with the experiments with TiO₂ alone. This suggests that the CNTs scaffolding network has facilitated the separation of photogenerated electron–hole pair in the composite films under the bias potential.

Carbon-doped TiO₂ coating on MWCNTs with high visible light photocatalytic activity was prepared by Cong et al [18]. The synthesis process consisted of two steps: the formation of TiC coated MWCNTs by molten salt method and the final formation of C-doped TiO₂ coated MWCNTs by controllable oxidation process. Because the TiO₂ coating on MWCNTs is prepared from oxidation of TiC, the coating is intimately contacted with the MWCNTs support and is expected to form chemical bonds with the MWCNT substrate. It is beneficial for the enhancement of the stability and the transfer of photogenerated electron between MWCNTs and conduction band of TiO₂ (figure 1). Furthermore, C-doped TiO₂ was formed owing to the diffusion of carbon to the surface of TiO₂ and the interface of TiO₂ and MWCNTs, which has been proved favorable for improving the photocatalytic activity.

The photocatalytic activities of photocatalysts were evaluated by investigating the degradation of MB aqueous solution under the visible light irradiation. The following photocatalysts were selected for the comparison of their photocatalytic efficiencies: P25, TiO₂ nanofibres, mixture of P25 and MWCNTs, mixture of TiO₂ nanofibres and MWCNTs, and C-doped TiO₂ coating on MWCNTs. The TiO₂ nanofibres were obtained by the oxidation conversion under flowing air atmosphere at 400 °C for 5 h of the TiC nanofibres prepared via molten salt reaction from the mixture of MWCNTs and Ti powder with molar ratio 1:1. C-doped TiO₂ coating on MWCNTs was prepared from the oxidation of TiC coated MWCNTs with a C/Ti molar ratio 3:1 in molten salt system and oxidation under flowing air at 400 °C for 5 h. It was observed that C-doped coating on MWCNTs shows the highest decoloration rate of MB.

Li Puma et al [19] have prepared CNT/TiO₂ core–shell nanocomposites with tailored shell thickness, CNT content, and studied its photocatalytic and photoelectrocatalytic properties. The surfactant wrapping modified sol-gel method was applied to fabricate TiO₂ shell from different titania precursors: titanium ethoxide (TeOTi), titanium isopropoxide (TTIP) and titanium butoxide (TBT). A uniform and well-defined nanometer-scale anatase titania layer on individual MWCNTs was formed. The photocatalytic activities of nanocomposites prepared from the aforementioned titania precursors were evaluated by studying the degradation of MB. Control experiments showed that UV-A irradiation could not degrade MB. The degradation rate of MB in an irradiated suspension of composites follows the sequence CNT/TiO₂ (TBT) > CNT/TiO₂ (TeOTi) > CNT/TiO₂ (TTIP) ~ TiO₂. The activities of composites appear to be related to the thickness of the TiO₂ layer and not so much on CNT content or C-doping.

In order to investigate the photoelectrocatalytic activity of composite photocatalyst, they are immobilized on an electrode of the photoelectrochemical reactor. The anodic photocurrent generated upon irradiation of composite photocatalyst film under the simultaneous application of a positive bias is related to the ability of the photocatalyst to shuttle away photoexcited electrons through the external circuit of an appropriated electrochemical cell. In other words, electrochemically assisted photocatalysis is an eloquent way to
minimize the charge recombination rates, provided that the system possesses sufficient conductivity for the effective application of an external bias. The experiments show that photocurrent density correlates in the same ascending order as the CNT content of the composites. In the case of photocurrent and photocatalytic activity, the thickness of the TiO$_2$ layer is not critical since charge separation is not driven by spontaneous transfer of electrons to CNT but by their migration to the anode collector due to the application of an external field to the photocatalyst via the extensive conductive network of CNTs. Thus the key parameters governing the behavior of a suspended photocatalytic system differ from those of a photoelectrochemical system in which CNT/TiO$_2$ composite are immobilized on a conductive support. The thickness of TiO$_2$ layer dominates the transport of electrons towards the CNTs core when the catalyst is applied in a slurry suspension and CNT network acts as an electron sink. However, the effectiveness of the photoelectrochemical method depends on the rate of electron removal which is controlled by the conductivity of the immobilized catalyst film. This conductivity increases with increasing CNT content.

For the application to the photocatalytic remediation of agro-industrial wastewaters Lopes et al.[20] have prepared CNT/TiO$_2$–CeO$_2$ photocatalytic nanocomposites by means of the surfactant wrapping modified sol-gel technique. At the beginning the CNT–TiO$_2$ nanocomposite was prepared, then it was immersed in the deposition solution for 2 h in order to allow the diffusion of plating solution into MWCNTs. The CeO$_2$ NPs were deposited on CNTs by means of the electrodeposition process. The electrodeposition was carried out at −15 V (versus Ag/AgCl) for 2 min and terminated after the total charge achieving 50 mC cm$^{-2}$. Nanocomposites with different molar proportion of CNT, TiO$_2$ and CeO$_2$ were prepared, then the samples were cured at different calcination temperatures within the range 300–700 °C. The photocatalytic oxidation was performed in a hollow cylindrical glass reactor.

Six phenol-like compounds were used to replicate the biologically refractory behavior of agro-industrial wastewaters: syringic, vanillic, 3, 4, 5-trimetoxybenzoic, veratic, protocatechuic and trans-cinnamic acid. For comparison purposes, adsorption and direct photocatalysis were accomplished to evaluate the abatement efficiency of phenol-like pollutants across all of photo-oxidation experiments.

The concentration of phenol-like compounds in aqueous solution was determined by high performance liquid chromatography HPLC. The photodegradation activity of the phenol-like pollutants was quantified in terms of total organic carbon (TOC) abatement. It was shown that the best photocatalyst is CNT$_{0.5}$/(TiO$_2$)$_{0.5}$–(CeO$_2$)$_{0.5}$. In brief, the performed experiments showed that carbon nanotubes and pure titania are not able to efficiently mineralize phenol-like pollutants. For the remediation of agro-industrial wastewater, several CNT/TiO$_2$–CeO$_2$ nanocomposites have been prepared with different molar proportions to photodegrade their organic content. In terms of parent compound conversion and TOC depletion, the best nanocomposite CNT$_{0.5}$/(TiO$_2$)$_{0.5}$–(CeO$_2$)$_{0.5}$ exhibited photocatalytic detoxification rates higher than 88% and 60%, respectively. From the long-term performance viewpoint, the CNT$_{0.5}$/(TiO$_2$)$_{0.5}$–(CeO$_2$)$_{0.5}$ catalyst was reutilized during five photo-oxidation runs exhibiting practically the same pollutant removal efficiency, thereby presenting an efficient nanocomposite for the environmental detoxification of phenolic wastewaters.

Takenaka et al.[21] have fabricated a specific nanocomposite for the photocatalytic degradation of organic compounds in water by depositing TiO$_2$ nanoparticles on CNTs and Pt nanoparticles in the CNT cavity of TiO$_2$–CNT composite. By means of the hydrolysis of titanium tetraisopropoxide in the presence of urea the outer surface of CNTs were uniformly covered by TiO$_2$ nanoparticles while, on the contrary, CNT surfaces were exposed if TiO$_2$–CNT composite was prepared without using urea. The urea added during the hydrolysis acted as a linker molecule to enhance the interaction between TiO$_2$ nanoparticles and CNTs. The photodegradation of acetic acid was performed over different TiO$_2$–CNT composites to clarify their catalytic activity. TiO$_2$–CNT (urea) with TiO$_2$ loading of 73 wt% and TiO$_2$–CNT (without using urea) with TiO$_2$ loading of 65 wt% were used as photocatalysts. It was observed that the catalytic activity of TiO$_2$–CNT (urea) was higher than that of both a mixture of TiO$_2$ and CNT as well as TiO$_2$–CNT composite (without using urea).

TiO$_2$ photocatalysts are frequently deposited on CNT surfaces in order to retard the recombination of photogenerated electron–hole pairs in TiO$_2$. Photogenerated electrons are transferred into CNTs. However, the photogenerated electrons on CNTs cannot be utilized efficiently for photocatalytic reactions, because the graphene surface, in general, shows poor activity for catalytic reactions. Therefore TiO$_2$–CNT (urea) samples were modified by depositing Pt nanoparticles in the CNT cavity of TiO$_2$–CNT (urea) composite. Then the electrons photogenerated in TiO$_2$ are transferred to Pt nanoparticles through CNTs and the electrons on the surface of Pt nanoparticles participated in the catalytic reactions. Simultaneously, the reaction involving the photogenerated holes occurred on the TiO$_2$ nanoparticles in the TiO$_2$–CNT (urea) composite can take place. The photodegradation of methanal, propanal, butanal and hexanal was carried out over TiO$_2$–CNT@Pt (urea) to clarify their catalytic performance.

### 3. Photocatalytic nanocomposite comprising titania and graphene or graphene oxide

In the present section we review some recent important research works on the photocatalytic nanocomposites comprising titania nanoparticles and graphene or graphene oxide nanosheets. Stengl et al.[22] have fabricated a large quantity of graphene nanosheets from natural graphite by using high-intensity cavitation field in a high-pressure ultrasonic reactor,
then used a well-defined quantity of graphene nanosheets to prepare a nonstoichiometric titania-graphene nanocomposite by thermal hydrolysis of suspension with graphene nanosheets and titania-peroxo complex. Graphene nanosheets with high specific surface area and unique electronic properties were used in this nanocomposite as good supports for TiO₂ to enhance the photocatalytic activity.

The thermal hydrolysis of the titania-peroxo complex generates spindle-like particles. The direct interaction between TiO₂ nanoparticles and graphene sheets prevents the reaggregation of the exfoliated sheets of graphene. Thanks to the presence of H₂O₂, graphene nanosheets are in part oxidized to graphene oxide nanosheets, and Ti³⁺ ions are formed. The presence of Ti³⁺ ions is the origin of the blue coloration which increases with increasing amount of graphene in the solution.

The graphene nanosheets play two roles in the nanocomposite. First, they make Ti³⁺ ions stable in the TiO₂ matrix, and second, they form heterojunctions with titania. Graphene works as sensitizer, and TiO₂ works as a substrate in the heterojunction system. Under UV and visible light irradiation, photoinduced electrons on titania surface can easily transfer to graphene nanosheets and, analogously, photoinduced holes on the graphene surface would migrate into titania. In this way, the photogenerated electron hole pairs in the catalyst are effectively separated, the probability of the electron–hole recombination is reduced and the photocatalytic activity increased. Moreover, due to the increase of Ti³⁺ concentration occurring as a result of the valence change of Ti ion from Ti⁴⁺ to Ti³⁺, surface states act as photocatalytic active sites in the TiO₂ surface.

Jiang et al [23] have synthesized a novel anatase TiO₂-graphene nanocomposite with exposed [001] high-energy facets by the hydrofluoric acid and methanol joint assisted solvothermal reactions. During the synthesis process, graphene was uniformly covered by a large number of anatase TiO₂ nanoparticles (20–25 nm) exposing the [001] facets. Methylene blue (MB) was used for evaluating the photocatalytic activity. Experiments have shown that the novel anatase TiO₂-graphene nanocomposite exhibits the highest photocatalytic activity compared to that of degussa P25 and highly reactive (HR) titana: the average degradation rate of MB within 60 min is 85.2% on this novel photocatalyst, 40.8% on P25 and 65.5% on HR-TiO₂. The high photocatalytic activity can be attributed to two crucial factors: the high charge separation rate based on the electron transfer and the effective exposure of highly reactive [001] facet of TiO₂.

In the experiments of Yu et al [24] the mesoporous titania-graphene photocatalytic nanocomposites were fabricated in high field via two successive steps: (i) hydrothermal hydrolysis of Ti(SO₄)₂ in an acidic suspension of graphene oxide (GO) to obtain TiO₂-GO nanocomposites and (ii) UV-assisted photoeduction of GO to get titania-graphene nanocomposites. The anatase TiO₂ nanocrystals with the crystallite size of 10–20 nm are densely packaged and supported on messy graphene sheets with close interfacial contacts. The adsorption and photocatalytic decomposition of mixed methyl orange (MO) and methylene blue (MB) dyes was conducted in aqueous solution containing titania-graphene nanocomposite samples at ambient temperature. In general, the pure TiO₂ shows no absorption above its fundamental absorption edge (around 400 nm). In contrast, the titania-graphene nanocomposites exhibit increased absorption in the visible region with increasing loading of graphene along with the color changing from white to gray. Notably, after the photocatalytic partial reduction of GO, the visible light absorption of the resulting TiO₂-G nanocomposites is somewhat higher than that of TiO₂-GO counterparts. Overall, although the visible light absorption of the titania-graphene nanocomposites increases as the loading amount of graphene increases, there is almost no change in the UV light absorption and no shift of the absorption edge. Thus the change in the absorption spectrum is not a dominant factor affecting the photocatalytic performance of as-prepared TiO₂-G nanocomposites.

The adsorption behavior of MO and MB on TiO₂-G and TiO₂ surfaces was investigated. Both MO and MB showed a slight adsorption on TiO₂. In contrast, the incorporation of graphene significantly enhances the adsorption capacity of both MO and MB, and in general, the adsorption capacity increases with increasing graphene incorporation. In particular, on TiO₂-G with 2 wt% of graphene, about 80% of MO and 90% of MB dyes were adsorbed.

The photocatalytic reactivity and selectivity of TiO₂-G nanocomposites were studied by monitoring the decolorization process of a mixed dye aqueous solution containing both MO and MB dye on there nanocomposites under UV light irradiation. MO and MB were chosen as model pollutants because their adsorption spectra almost do not overlap and their characteristic absorption are well separated, when graphene is coupled with titania the photogenerated electrons can easily transfer to graphene leading to the efficient separation and prolonged recombination time of electron–hole pairs. This phenomenon together with promoted reactant adsorption enhance the photocatalytic activity of titania-graphene composite.

In another work by Yu et al [25] the hierarchical macro/mesoporous titania-graphene nanocomposites with low graphene loading (0–0.20 wt.%) were prepared by hydrothermal treatment of graphene oxide (GO) and hydrolyzates of tetrabutyl titanate (TBOT) in an ethanol-water solvent. The photocatalytic activity of the as-prepared titania-graphene powders and degussa P25 was studied by investigating the oxidation decomposition of acetone in air at ambient temperature. Photocurrents were measured by using an electrochemical analyzer in a standard three-electrode system with as-prepared samples as the working electrode and Ag/AgCl (saturating KCl) as the reference electrode. It was shown that the graphene content has a great effect on the photocatalytic activity of TiO₂. The hierarchical macro/mesoporous structure is beneficial for enhancing the adsorption efficiency of light and the flow rate of the gas molecules. After introducing a small amount of graphene the photocatalytic activity...
activity of the nanocomposite remarkably enhanced: at 0.05 wt% graphene content the enhancement factor is 1.7 for fine TiO$_2$ and 1.6 for P25. However, the further increase of graphene content leads to the decrease of the photocatalytic activity due to the increases of the opacity of the samples and also because the excess loading of graphene prevents the light to reach the TiO$_2$ surface.

The major reactions in the photocatalytic process under UV light radiation are:

\[
\text{TiO}_2 / \text{graphene} \xrightarrow{h
u} \text{TiO}_2 (h^+) + \text{graphene} (e^-),
\]

\[
\text{graphene} (e^-) + O_2 \rightarrow \text{graphene} + \cdot O_2^-,
\]

\[
\text{TiO}_2 (h^+) + \text{OH}^- \rightarrow \text{TiO}_2 + \cdot \text{OH},
\]

\[
\text{CH}_3\text{COCH}_3 + 4\cdot\text{OH} + 3\text{O}_2 \rightarrow 3\text{CO}_2 + 3\text{H}_2\text{O}.
\]

To further confine the above suggested photocatalysis mechanism, the transient photocurrent responses were recorded. It was shown that the photocurrent value of TiO$_2$ rapidly decreases to zero when the UV light is switched off, and the photocurrent occurs back to a contant value when the light is on again. However, in the case of titania-graphene composites, the photocurrent value gradually increases to a constant value when the light is switched on and gradually decreases to zero when the light is switched off. The above presented phenomenon demonstrated that in the titania-graphene nanocomposites the photogenerated electrons on the conduction band of TiO$_2$ tend to transfer to graphene sheets [26, 27]. Therefore the photocurrent is generated by stored electron transferred from the conduction band of TiO$_2$ directly. When the light is switched off, due to the electron storage effect of graphene, electrons were gradually released from graphene sheets and further transferred to working electrode, leading to the gradual decrease of photocurrent to zero.

Silica-based ordered mesoporous materials are excellent supports of photocatalysts due to their large surface area and flexible pore size. Li et al [28] have prepared ordered mesoporous graphene-titania/silica composite material for the photodegradation of aqueous pollutants under the Sun-light irradiation by means of a direct sol-gel co-condensation technique combined with hydrothermal treatment in the presence of a triblock copolymer non-ionic surfactant P123. The composite exhibited a two-dimensional hexagonal p6 mm symmetry and anatase phase structure with a large Brunauer–Emmet–Teller surface area and uniform pore size. The photocatalytic activity of the prepared graphene-titania/silica (GTS) nanocomposite with titania/silica (TS) proportion 4:1 and 1 wt.% graphene content, denoted GTS(4:1)-1%, was evaluated investigating the photodegradation of two typical organic pollutants, atrazine and rhodamine B, under the irradiation by simulated sunlight on this sample. For the comparison other sample such as pure TiO$_2$, GT-1%, TS(4:1) and GTS(4:1)-1% -disorder were also tested.

In the direct photolysis of atrazine and rhodamine B under simulated sunlight, the decrease of their concentration is negligible. Compared with pure TiO$_2$, the photocatalytic activities of GT-1% and TS(4:1) are higher, and the ordered mesoporous GTS(4:1)-1% composite is the most photoactive among all tested materials. On this catalyst the degradation of atrazine reached 93.1% after 180 min of irradiation, and the total degradation of rhodamine B was achieved after 30 min of irradiation. Additionally, the photocatalytic activity of the ordered mesoporous GTS(4:1)-1% composite is higher than that of GTS(4:1)-1%-disorder.

It is easy to explain the mechanism of the increase of photocatalytic activity when graphene was used to form a nanocomposite together with an oxide semiconductor such as TiO$_2$ or the TS composite: graphene transferred or/and trapped electrons photogenerated in the oxide semiconductor, leaving the holes to form the reactive species (figure 2). Therefore the charge recombination was suppressed, leading to the improvement of the photocatalytic performance.

Nanocomposites comprising titania and reduced graphene oxide (rGO) were prepared by Yoo et al [29] by a simple one–step hydrothermal reactions using titania precursor, Ti-Cl$_4$, and graphene oxide (GO) without reducing agents. Hydrolysis of Ti-Cl$_4$ and mild reduction of GO were simultaneously carried out under hydrothermal conditions. While conventional methods often utilized reducing toxic agents, the method of this work does not use toxic solvents.

Graphene oxide was prepared from graphite powder using a modified Hummer’s method [30, 31]. TiO$_2$-rGO composite was synthesized by simultaneously carrying out the reduction of GO, hydrolysis of TiCl$_4$ and crystallization of produced TiO$_2$ in a single-step hydrothermal reaction. The photocatalytic activity of the as-prepared composite catalyst was studied by investigating the photodegradation of a rhodamine B (RhB) solution under the irradiation by visible light at the ambient temperature. For the comparison, the photocatalytic activity of P25 is studied under the same reaction conditions. The authors have obtained following result.

Without catalyst and in the presence of rGO, under the visible light irradiation there was almost no change of the concentration of rhodamine B. However, the photodegradation was evidently observed in the presence of TiO$_2$-rGO.
nancopolyst catalyst. Following degradation mechanism was proposed [32]:

\[
TiO_2 + rGO \xrightarrow{h^+} TiO_2(h^+) + rGO (e^-),
\]
\[
rGO(e^-) + O_2 → rGO + O_2^-, 
\]
\[
TiO_2(h^+) + H_2O/OH^- → TiO_2 + *OH,
\]
\[
*OH + RhB → degradation products.
\]

The photocatalytic efficiency reached its maximum at 2 wt% rGO concentration, resulting in rhodamine B degradation of 98.8 wt% after 80 min of visible light irradiation.

A visible light active photocatalyst comprising Fe-doped TiO₂ nanowire arrays grown on the surface of functionalized graphene sheets (FGSS) as the templates was fabricated and studied by Charpentier et al. [33]. A sol-gel method in supercritical carbon dioxide (scCO₂), a green solvent, was applied. scCO₂ facilitated Fe doping in TiO₂ and was used to enhance the exfoliation of graphene sheets. Photodegradation of 17β-estradiol (E2) as a model endocrine disrupting compound (EDC) was investigated under visible solar irradiation (λ ≥ 420 nm).

The photocatalytic activities of different Fe-doped (0%, 0.20%, 0.40%, 0.60% and 0.80%) TiO₂ nanowire/graphene sheets and also of Fe-doped TiO₂ were evaluated by investigating photodegradation of E2 in aqueous solution under visible light irradiation. It was observed that there was no photodegradation of E2 in the presence of only pure nano TiO₂ under the visible irradiation, as expected, and the degradation rate under the visible irradiation increased with increasing Fe doping level. Moreover, Fe-doped TiO₂ nanowire/graphene assemblies show higher photocatalytic activity compared to that of Fe-doped TiO₂ without graphene. The increase of photocatalytic activity is the result of the enhancement of pollutants adsorption to graphene surface and the red shift of the absorption spectrum.

A charge transfer mechanism in Fe-doped TiO₂/FGO nanocomposites was proposed: the FGOs have a work function around 4.2–4.5 eV, in which excited electrons from Fe-doped TiO₂ anatase conduction band can transfer to its (FGSS) conduction band, resulting in narrowing the band gap, reduction of photoluminescence intensity, charge separation, stabilization and hindering charge recombination. Moreover, Fe-doped TiO₂/graphene photocatalysts can absorb more visible light leading to the increase of the photocatalytic activity under the visible light irradiation. In addition, when Fe-doped TiO₂ nanowire were grown on the surface of graphene sheets, higher surface area photocatalysts were obtained: pollutant (E2) molecules were trapped on the graphene pore, then Fe-doped TiO₂ nanowires degrade them more efficiently.

In the experimental work of Silva et al. [34] a valuable comprehensive study of graphene oxide−TiO₂ photocatalytic nanocomposite has been performed towards investigating and optimizing the assembly and interfacial coupling of TiO₂ nanoparticles on graphene oxide (GO) sheets, exploiting the in situ liquid phase deposition followed by thermal reduction in N₂ atmosphere. Reduced graphene oxide−TiO₂ (GOT) composites were prepared by liquid phase deposition followed by post-thermal reduction at 200 °C and 350 °C. The photocatalytic activity of the material was evaluated by investigating the degradation of diphenhydramine (DP), an important pharmaceutical water pollutant, and methyl orange (MO), an azo-dye, under both near UV−vis and visible light irradiation.

The dependence of photocatalytic activity on GO content was evidenced. In particular, under visible light irradiation the optimum photocatalytic performance was attained for the composites treated at 200 °C and comprising 3.3–4.0 wt% of GO due to optimal assembly and interfacial coupling between reduced graphene oxide (rGO) sheets and TiO₂ nanoparticles. Almost total degradation and significant mineralization of DP and MO pollutants (in less than 60 min) was achieved under near UV/Vis irradiation for the optimum GOT structure exhibited a porous structure with a high surface area.

Photocatalytic experiments employing sacrificial holes and radical scavenging agents revealed that photogenerated holes are the primary active species in DP degradation for both bare TiO₂ and GOT under UV/Vis irradiation, while an enhanced contribution of radical mediated DP oxidation was envisaged under visible light. These results together with the quenching of the GO photoluminescence under visible and near infrared laser excitation indicate that rGO acts either as electron acceptor or electron donor (sensitizer) of TiO₂ under UV and visible light.

A particular graphene-TiO₂ composite photocatalyst comprising ultrathin anatase TiO₂ nanosheets grown on graphene nanosheets with dominating [001] facets was fabricated by Xu et al [35]. The photocatalytic activity of the products was studied by investigating the degradation of methylene blue (MB) under visible light irradiation at λ ≥ 400 nm. The results showed that the TiO₂/graphene nanosheets exhibit much higher photocatalytic activity in comparison with pure TiO₂ and P25: 82.5% of MB is degraded by TiO₂/graphene nanosheets within 1 h irradiation while that of pure TiO₂ is about 35.5% and for P25 almost 82.2% of MB remains in the solution.

The enhancement of photocatalytic activity is achieved due to following three factors:

First, the TiO₂/graphene nanosheets exhibited an obvious red shift of the absorption spectrum and higher absorbance in the visible region. Thus, the incorporation of graphene improved the absorption of visible light.

Second, the conduction band of TiO₂ is more negative than the work function of graphene, such that the transfer of photogenerated electrons from TiO₂ to graphene is energetically favorable. Thus, graphene as an acceptor of electrons inhibited the charge recombination, and there were more charge carriers to promote the degradation of dyes. Moreover, graphene has excellent conductivity and rapid transport of charge carriers facilitated the charge transfer. Overall, both the electron accepting and transporting properties of graphene in TiO₂/graphene composites effectively suppressed the electron−hole recombination and enhanced the photocatalytic activity.
Third, the interfacial electron transfer is mediated by the surface defects, and the separation of photogenerated electron–hole pairs is accelerated by the [001] facets. Significantly, in TiO$_2$–graphene composites, ultrathin anatase TiO$_2$ nanosheet enwrapped [001] facets can be produced.

In reference [36] Wang et al have investigated the visible light photocatalytic activity of graphene@TiO$_2$ ‘dyade’–like structure and observed the reduction of charge carriers recombination and the enhancement of reactivity. For comparison the photocatalytic performances of graphene, pure TiO$_2$, graphene-TiO$_2$ physical mixture and graphene@TiO$_2$ ‘dyade’ were investigated by studying the photodegradation of methylene blue (MB) under the irradiation by UV and visible lights ($\lambda > 450, 590$ and $700 \text{ nm}$). It was shown that graphene@TiO$_2$ had the anatase phase and was able to absorb a high amount of photoenergy in the visible light region and to drive effectively photochemical degradation reaction. There were more *OH radicals generated on graphene@TiO$_2$ (1:3) than on pure TiO$_2$ under the irradiation by both UV and visible lights ($\lambda > 450, 590$ and $700 \text{ nm}$). It was shown that graphene@TiO$_2$ had the anatase phase and was able to absorb a high amount of photoenergy in the visible light region and to drive effectively photochemical degradation reaction. There were more *OH radicals generated on graphene@TiO$_2$ (1:3) than on pure TiO$_2$ under the irradiation by both UV and visible lights, and MB was eliminated mainly by means of *OH radical oxidation. According to the experimental data, the graphene@TiO$_2$ ‘dyade-like’ structure exhibits significantly enhanced photodegradation of MB compared to graphene, pure TiO$_2$ and graphene-TiO$_2$ physical mixture (1:3) and achieves highest efficiency at the mass ratio graphene:TiO$_2$ = 1:3. Under UV light irradiation, about 88% MB is decomposed by the graphene@TiO$_2$ (1:3) after less than 100 min, while 60–70% MB still remains in the solution after the same time period if pure TiO$_2$ and physical mixture of graphene and TiO$_2$ (1:3) are used.

Kamat et al [37] have designed a particular photocatalytic material comprising TiO$_2$ and Au nanoparticles (NPs) anchored on reduced graphene oxide (rGO) sheets. The synthesis process was performed as follows. At the beginning TiO$_2$ and Ag NPs were deposited on graphene oxide (GO) sheets and the resultant composite material was dissolved in deaerated ethanol. Then TiO$_2$ NPs were irradiated by UV light ($\lambda < 320 \text{ nm}$) to generate mobile electrons and holes:

$$hv + TiO_2 \rightarrow TiO_2^+ + e^- + h^+. $$

The holes were transferred to ethanol and the electrons were trapped at Ti$^{3+}$ sites:

$$e^- + h^+ + TiO_2 + C_2H_5OH \rightarrow TiO_2 (e^-) + C_2H_5OH^+. $$

The trapped electrons were transferred to GOx and reduced GO to form rGO:

$$TiO_2 (e^-) + GO \rightarrow TiO_2^-rGO ,$$

while reaction between C$_2$H$_5$OH$^+$ and GO also led to the formation of GO:

$$C_2H_5OH^+ + GO \rightarrow TiO_2^-rGO (e^+) + products. $$

Then electrons stored in rGO reduced Ag$^+$ ions to form Ag NPs:

$$TiO_2^-rGO (e^+) + Ag^+ \rightarrow TiO_2^-rGO (e^-)/Ag. $$

Thus the rGO mediated reduction is efficient for depositing Ag NPs on rGO, but the similar procedure cannot be applied to reduce Au$^{3+}$ ions and to deposit Au NPs. It is because the conduction electron in TiO$_2$ is energetic enough to reduce both Ag$^+$ and Au$^+$ ions in suspension, but electrons transferred to GO are energetic enough to reduce only Ag$^+$ and not Au$^{3+}$ ions. It was proposed to use redox chemistry to replace Ag with Au$^{3+}$ on the basis of galvanic exchange principle. By mixing AuCl$_4^-$ solution with TiO$_2$–rGO/Ag dispersion, Ag NPs deposited on rGO were transformed to Au NPs:

$$TiO_2 - rGO/Ag + AuCl_4^- \rightarrow TiO_2 - rGO/Au + Ag^+ + 4Cl^-.$$

In brief, the authors have succeeded in designing a hybrid photocatalytical material by anchoring TiO$_2$ and metal (Ag and Au) NPs onto rGO. rGO platform improves the large separation by suppressing recombination in TiO$_2$ and therefore enhances the photocatalytic activities. Using methyl viologen as a probe, the authors have elucidated the mechanisms of the photocatalytic process.

Graphene oxide (GO)-TiO$_2$ microsphere hierarchical membrane for clean water production was fabricated by Siu et al [38], through assembling GO-TiO$_2$ microsphere composite on the surface of a polymer filtration membrane. It consists of hierarchical TiO$_2$ microsphere as photocatalyst and GO sheet playing the double role of cross-linker for individual TiO$_2$ microspheres and electron acceptor for enhancing photocatalytic activity. This kind of membrane possesses the multifunction of simultaneous water filtration and pollutant degradation. Compared to previous ceramic membranes GO-TiO$_2$ microsphere membrane possesses two advantages: (1) sustainably high water flux due to the alleviation of membrane fouling by hierarchically porous membrane structure, and (2) enhanced strength and flexibility from the cross-linking effect of GO sheet. To demonstrate the engineering applicability of GO-TiO$_2$ membrane for water purification, the flux performance of GO-TiO$_2$ membrane was investigated in a lab-scale set up.

The photodegradation activity of GO-TiO$_2$ was studied by investigating the degradation of RhB and AO7 which are the major pollutants from textile industry. The TiO$_2$ membrane itself has limited efficiency in removing dye: less than 15% of RhB and AO7 can be removed by membrane filtration process without UV irradiation. UV light itself also can degrade only less than 50% of RhB and AO7. Experiment showed that GO-TiO$_2$ membrane shows higher photodegradation efficiency: RhB and AO7 dyes are totally degraded within 30 and 20 min by GO-TiO$_2$ membrane under UV irradiation, respectively. The efficient photocatalytic activity plays a significant role in eliminating membrane fouling, because less organics and macromolecules can be accumulated on the GO-TiO$_2$ membrane surface, which guarantees longer working time of GO-TiO$_2$ membrane compared to traditional ones.

The photocatalytic multilayer nanocomposites consisting of graphene oxide (GO) as well as reduced graphene oxide (rGO) sheets and TiO$_2$ nanoparticles deposited at different contents (1–10%) on these sheets were fabricated and investigated by Ismail et al [39]. The fabrication method in this
work has several advantages: (i) there was no extra reducing agent, (ii) the \textit{in situ} growth of TiO$_2$ nanoparticles leads to the formation of uniform nanoparticles located on rGO sheets, and (iii) TiO$_2$–rGO multilayers are capable of high diffusion and adsorption of dyes.

In the performed fabrication method, TiO$_2$–rGO nanocomposites were prepared by heat treatment of TiO$_2$–GO nanocomposites at 450 °C. The photocatalytic activities of fabricated nanocomposites and of pure TiO$_2$ were assessed by investigating the photodegradation of aqueous solutions of methylene blue (MB). Experiments showed that the photocatalytic degradation rate of MB by TiO$_2$–rGO nanocomposite is 6 and 2 times larger than those of TiO$_2$–GO nanocomposite and pure TiO$_2$, respectively.

One of the effective methods to improve the photocatalytic activity of TiO$_2$ is the addition of reduced graphene oxide (rGO) to TiO$_2$. In reference [40] of Lei \textit{et al} the easily recycled TiO$_2$–rGO nanocomposites were fabricated by a one-step green hydrothermal method based on the initial formation of strong-coupling TiO$_2$–GO nanocomposites and the subsequent \textit{in situ} reduction of GO to rGO during hydrothermal treatment in pure water without using any reductant and surfactant. Owing to the large specific surface area of graphene and the excellent mobility of charge carriers, the addition of graphene is one of the effective methods to improve the photocatalytic performance of TiO$_2$. The performance of fabricated TiO$_2$–rGO photocatalyst was evaluated by investigating the degradation of phenol under the irradiation by UV light.

When the amount of rGO increase to ca. 1 wt%, the photocatalytic performance is enhanced by a factor of 23%. This increase of photocatalytic activity can be attributed to the cooperation effect of the effective separation of charge carriers via rGO cocatalyst, the enrichment of phenol molecules on the rGO and the strong-coupling interaction between TiO$_2$ nanoparticles and rGO nanosheets. However, with further increase of graphene content the photocatalytic activity of the TiO$_2$–rGO nanocomposites decreases. The possible reasons of this decrease are the opacity and light scattering of the material, and high graphene load shielding the TiO$_2$ from absorbing UV light.

Photocatalytic materials comprising TiO$_2$–nanocarbon composites immobilized into hollow fibres were studied by Silva \textit{et al} [41]. Nanocarbons in three different forms were used: carbon nanotube (CNT), fullerene (C$_{60}$) and graphene oxide (GO). Composites corresponding to two different carbon contents (4 wt% and 12 wt%) were synthesized by the liquid phase decomposition method and tested in photocatalytic experiments under both near–UV/Vis and visible light irradiation in the form of powder slurries, then were immobilized into application. The photocatalytic experiments consist of 4 steps: (1) pollutant adsorption in dark phase, (2) photocatalytic degradation of diphenyldiurethane pharmaceutical (DP), (3) photocatalytic degradation of methyl orange azo-dye compounds (MO) and (4) immobilization of GO–TiO$_2$ composite into hollow fibres.

Preliminary experiments under dark conditions were performed to establish the adsorption-desorption equilibrium of the pollutants at room temperature (25 °C). For DP the adsorption capacity was around 7%, 4% or 3% for GO-TiO$_2$, CNT-TiO$_2$ and C$_{60}$-TiO$_2$, respectively, at carbon contents 4 wt% and 15%. 7% or 5% at carbon content 12 wt%. For MO the highest adsorption capacity was obtained with GO-TiO$_2$: 8% and 15% at carbon content 4% and 15%, followed by CNT-TiO$_2$ and then C$_{60}$-TiO$_2$. Overall, adsorption was always lower than 15% of the initial pollutant concentration, indicating that adsorption in the dark will contribute only to a slight removal of the pollutants during the adsorption–desorption process.

In the experiments on photocatalytic degradation of DP, among the photocatalysts containing 4 wt% of carbon, the highest photocatalytic performance under near–UV/Vis irradiation was found for GO-TiO$_2$, but when the GO content increased to 12 wt%, the photocatalytic activity significantly decreased. In contrast with GO-TiO$_2$ composites, the photocatalytic activities of composites containing 12 wt% of CNT and C$_{60}$ are higher than those of composite containing 4 wt%. Overall, GO–TiO$_2$ achieved highest photocatalytic activity for DP degradation under both near–UV/Vis and visible light irradiation at the carbon content of 4 wt%. The experiments on MO degradation showed that when the carbon content increased from 4 wt% to 12 wt% the photocatalytic activities of all three composites decreased, and GO-TiO$_2$ composite at carbon content of 4 wt% possessed highest activity. The different photocatalytic efficiencies of the photodegradation of DP and MO indicated that the activity depends on the kind of the target pollutant. In fact, the photocatalytic mechanism for DP is mediated by hole and therefore is more important than that of photoreduction mediated by electron for MO.

Since the use of photocatalysts in the powder form was associated with many drawbacks including the difficult separation of the catalyst from the treated influent, GO-TiO$_2$ composite was immobilized into the matrix of alginate porous hollow fibres for the practical application.

In reference [42] Sim \textit{et al} have fabricated a photocatalytic nanocomposite by a two-phase method: dissolve CdS nanoparticles in toluene and mix resultant substance with graphene oxide (GO) aqueous solution. CdS nanoparticles were uniformly self-assembled on GO sheets at water/toluene interface. GO-CdS composite has advantages of both components and acquires more benefits than previous CdS involved photocatalysts, including: (i) uniform distribution of CdS nanoparticles on GO sheets facilitating charge transfer and reducing electron–hole recombination rate, (ii) easy recovery of this composite due to the large size of GO sheets, (iii) excellent contact between CdS nanoparticles and GO sheets preventing CdS from leaching out.

The photocatalytic activity of GO-CdS nanocomposite was investigated by studying the degradation of AO7, MB, RhB under visible light irradiation. Over 80% of AO7 is degraded by GO-CdS composite, while only 50% of AO7 is decomposed by pure CdS nanoparticles within 60 min. Note that the concentration of AO7 has almost no change under visible light irradiation without any photocatalysts. Moreover, very little Cd$^+$ (ca. 3.5%) is leached out from GO-CdS nanocomposite, while pure CdS nanoparticles are suffered.
from severe photocorrosion (ca. 38.6% Cd⁺ is leached out), which is a common problem for pure CdS photocatalysts. GO-Cds nanocomposite also exhibits much higher efficiency in degradation of MB and RhB.

GO-Cds nanocomposite shows also enhanced antibacterial activity compared to CdS nanoparticles as well as to GO. Note that visible light itself does not have enough energy to kill E. coli. GO has also limited capability in inactivating E. coli whereas GO-Cds kills 100% E. coli in 25 min. Beside gram-negative E. coli, the antibacterial activity of GO-CdS nanocomposite with respect to gram-positive B. subtilis was also investigated. Around 90% B. subtilis was killed by GO-Cds nanocomposite in 10 min, while 60% B. subtilis was survived after being treated with pure CdS. Since both CdS and GO-CdS exhibit low capability in inactivating E. coli and B. subtilis under dark condition, the influence of toxicity of CdS can be neglected.

The transient photocurrent measurement and radical scavenger investigation show that the efficient photo-degradation and disinfection activities are originated from *OH radical generated by GO-Cds nanocomposite under visible light irradiation.

In reference [43] Yan et al prepared a series of graphene/TiO₂ composites by a single-step method using nonionic surfactant combined with solvothermal treatment technique. These composites were successfully applied to degrade typical aqueous persistent organic pollutants such as rhodamine B, aldicarb and norfloxacin under the illumination by simulated sunlight (λ > 320 nm) and visible light (λ > 400 nm). The degradation mechanism was studied. It was shown that graphene plays the role of acceptor of photogenerated electrons from TiO₂ and effectively suppresses the recombination of electron–hole pairs. The surface defects of TiO₂ lattice can also enhance the quantum efficiency of the photocatalyst, because they reduce the electron–hole recombination probability. They prolong the lifetime of electrons and holes not only by trapping them, but also by transferring the trapped charges to reactants.

However, for high graphene loading, the aggregation of graphene nano-sheets is unfavorable to the separation of electron–hole pairs and the photocatalytic activity is reduced. In addition, the light-shielding effect of graphene with high graphene loading also causes the decrease of the photocatalytic activity.

The UV–vis spectra showed that the bandgap of graphene/TiO₂ composites narrowed compared with pure TiO₂ and this decrease of the bandgap resulted in the increase of photocatalytic activity of the material under the Sunlight and visible light irradiation. About 79.7% and 86.2% of total organic carbon (TOC) disappeared in graphene/TiO₂ 0.86% after 10 h of simulated sunlight irradiation for rhodamine B and norfloxacin degradation, but only about 36.8% of TOC disappeared in graphene/TiO₂–0.86% after 25 h of visible light irradiation for aldicarb degradation.

A magnetic TiO₂-graphene hybrid photocatalyst was fabricated by Luo et al [44] for the use in removal of herbicides from water. A simple sol-gel method combined with self-assembly was applied to obtain graphene supported core–shell magnetite@TiO₂ photocatalyst with a thin SiO₂ layer between the magnetic core and the TiO₂ shell (figure 3). This hybrid nanostructure intergrated four different functions: (1) enhanced photocatalysis, (2) excellent electron capture ability and high adsorptivity of graphene, (3) magnetic separation and (4) high stability through suppressing photodissolution of the magnetite by SiO₂. The photocatalytic activity, repetitive use and life time of the photocatalysts for degradation of typical herbicide 2, 4D in different water samples including real wastewaters were investigated. The chemical oxygen demand (COD) and toxicity assessment of the treated water samples also determined.

The adsorption capacities of photocatalysts were investigated by placing them in 2, 4D aqueous solutions for 0.5 h in the dark and evaluating the remaining 2, 4D concentration by HPLC. It was shown that the adsorption capacities of the catalysts with reduced graphene (RG) are about 25%, much higher than those (≤8%) of the catalysts without RG. Both the large specific surface area and the strong affinity of graphene towards organic molecules were responsible for the high adsorption capacity of RG–involved photocatalysts. Subsequently, the photocatalysts with adsorbed 2, 4D were irradiated with a xenon arc lamp for degrading all adsorbed 2, 4D molecules.

The investigation of photocatalytic degradation of 2, 4D in water by using MT@SiO₂@TiO₂–RG showed that almost 100% herbicide disappeared after 140 min of irradiating this hybrid photocatalyst, much higher than 33% in the case when P25 was used.

The toxicities of the treated water sample containing 2, 4D was evaluated by the inhibitory action on the growth of E. coli at different times. After 140 min irradiation the 2, 4D water sample showed negligible adverse effect on the growth of E. coli.

The repetitive use of MT@SiO₂@TiO₂–RG was studied. At the end of each cycle of completion of the degradation the used photocatalyst was collected through magnetic separation and then utilized for the next cycle. The results showed excellent recovery and reusability of the photocatalyst. The removal efficiency was still as high as 97.7% after 8 successive cycles, and notably the removal efficiency achieved 99.1% when the photocatalyst was re-treated by ultrasonication after 8 cycles.

In a recent interesting work of Xu et al [45] a non-covalent functionalization method was applied for controlled synthesis of ultralarge sandwich-like titania-graphene composite photocatalytic nanosheets. The photocatalytic activity of the prepared catalysts are evaluated by selective reduction of 4-nitroaniline (4-NA) to p-phenylenediamine (PPD) in the aqueous phase with the addition of ammonium formate as quencher for photogenerated holes and N₂ purge under UV light irradiation. The composite photocatalyst with 5 wt% content of graphene shows the best performance. Within 8 min the 4-NA is completely reduced to PPD with a high selectivity (99%, determined by high performance liquid chromatography). The efficiency of this best composite photocatalyst was then examined under the same conductions for a series of 8 substituted aromatic nitro compounds. In
addition, the stability of the synthesized composite was also evaluated. After 5 times recycling test for the selective reduction of 4-NA, the photocatalytic activity of the used material is almost the same as that of its fresh counterpart.

The photoluminescence (PL) of the prepared composite photocatalyst was investigated in order to clarify the role of graphene on promoting the photocatalytic activity. While the blank TiO₂ exhibits a broad emission peak around 500 nm under the band gap excitation, which is attributed to the charge recombination on the defect sites of TiO₂, the presence of graphene in the composites reduces the PL intensity, indicating the reduced charge carriers recombination compared to the blank TiO₂. This result is also supported by the photoelectrochemical measurements: the transient photocurrent response of the composite with 5 wt% of graphene content is much higher than that in blank TiO₂. On the basis of above presented results, a reaction mechanism was proposed. Under UV light irradiation, the electron–hole pairs are generated over TiO₂. Since the conduction band of TiO₂ is more negative than the work function of graphene, the photogenerated electrons can transfer from TiO₂ to graphene nanosheets, promoting the charge carriers separation. Simultaneously, the photogenerated holes are trapped by ammonium formate. In addition, the N₂ atmosphere provides an anaerobic condition for nitro reduction. The photogenerated electrons transferred to the adsorbed aromatic nitro compounds and the degradation took place.

In another recent work of Shi et al [46], a series of anatase-graphene-rutile heterojunction photocatalyst were fabricated by the surface-assembling method. The influence of the relative amounts of anatase (A), rutile (R) and graphene (G) on the photocatalytic activity of the prepared composites was systematically studied by investigating the hydrogen production. However, the photocatalytic degradation of pollutants could be also investigated in a similar manner.

In a recent interesting work of Kang et al [47] a new hybrid nanocatalyst comprising TiO₂ nanocomposite nanowires (CNWs) encapsulated with graphene (G) and palladium nanoparticles (Pd NPs) designated as G-Pd@TiO₂-CNWs was prepared and investigated. The preparation of this composite nanocatalyst involved two major steps: preparation of electrospun composite titane nanofibres by electrospinning and then by calcination of prepared composite titane nanofibres. The band gap energy (e.g.) required for the indirect transition of pristine TiO₂-CNWs and Pd or G-Pd-included TiO₂-CNWs was estimated from the plots of (αhv)² versus hv. It was shown that the e.g. value of G-Pd@TiO₂-CNWs, G@TiO₂-CNWs and Pd@TiO₂-CNWs was lower than that of pristine TiO₂-CNWs. An additional mid-band gap at 2.0 eV was present in Pd@TiO₂-CNWs and G-Pd@TiO₂-CNWs due to the effect of G, Pd or G-Pd into TiO₂-CNWs. This redshift of the band edge results in higher photocatalytic activities of the prepared hybrid nanocatalyst in the visible region.

The G-Pd@TiO₂-CNWs were utilized for the photoreduction of 4-nitrophenol (4-NP) under visible light irradiation. The practical utility of the G-Pd@TiO₂-CNWs photocatalyst for real industrial wastewater samples generated by the hair dye industry was investigated. The photocatalytic reduction of 4-NP in hair dye industrial wastewater was completed within 20 min and the solution turned colorless. This confirmed the real-time practical application of the
G-Pd@TiO2-CNWs photocatalyst for the reduction of 4-NP. Similarly, the G-Pd@TiO2-CNWs photocatalyst was employed for the reduction of 4-NP in an environmental water sample. The photocatalytic reduction efficiency of the G-Pd@TiO2-CNWs photocatalyst at 30 min for pond water, tap water and river water samples polluted by 4-NP were as follows: pond water (100%) >tap water (97.2%) >river water (80.5%).

By means of the one-step hydrothermal method Yang et al [48] have synthesized a platinum-based catalyst with a graphene-based porous matrix as the support. The prepared porous catalyst possessed following characterizing features: (i) platinum nanoparticles (Pt NPs) with an average size of 3.6 nm are uniformly distributed on the graphene sheets; (ii) the preparation of the platinum-based catalyst is realized through one-step hydrothermal synthesis which utilized almost 100% of the starting materials; (iii) the graphene-based porous matrix acting as the support for the platinum-based catalyst in benificial for fast ion transport during the electrocatalytic process.

The methanol oxidation reaction was used as the model reaction to investigate the catalytic performance of the as-prepared platinum-based porous catalyst. Electrochemical measurements demonstrated that the catalyst had a much stronger resistance to poisoning and a higher stability than the comercial Pt/C catalyst. It was shown that the optimum annealing temperature was 350 °C. The increased electrocatalytic activity of the prepared porous catalyst was ascribed to 5 factors:(1) faster electron transfer occured between Pt NPs and graphene matrix; (2) the oxygen-containing groups on the graphene sheets were responsible for the increased resistance to poisoning, because they played a major role in the removal of intermediate carbonaceous species; (3) the porous graphene matrix provided more paths for fast ion transport; (4) there was a uniform distribution of Pt NPs on the graphene matrix; (5) the graphene matrix had a macro-pore-dominant microstructure which was favorable for efficient fuel and product diffusion.

Chai et al [49] have applied the one-pot solvothermal method developed in their previous works [50, 51] to prepare the graphene–TiO2 (GT) nanocomposite from titanium (IV) butoxide and graphene oxide, and used this composite to fabricate the noble metal (NM)-reduced graphene oxide (rGO)-TiO2 ternary photocatalytic nanomaterial (NM-GT) by means of a simple polyol method without employing toxic and harsh reducing agents. Ethylene glycol was used as both the solvent and reducing agent for the additive metal ions to form metal (Pt, Pd, Ag, and Au) islands on the surface of TiO2 and rGO. Amongs the prepared samples that with Pt-GT displayed the highest efficiency for the reduction of CO2 into CH4 gas under the irradiation of low-power energy-saving daylight bulbs. The strong interaction between different components of the composites resulted in an efficient charge separation and improved utilization rate of visible light.

The photocatalytic activities of the developed NM-GT ternary nanocomposites was studied in a CO2 photoreduction system at ambient condition in a continuous gas flow reactor. The CO2 photoreduction process was performed under visible light irradiation with a maximum light intensity of 15 W. During the photocatalytic experiments, CH4 was detected as the sole product. The photocatalytic activity of CO2 reduction was found to follow the order Pt-GT > Pd-GT > Ag-GT > Au-GT > anatase TiO2. The optimum loading of Pt to achieved most efficient photocatalytic performance is that with the Pt:GT ratio equal to 2 wt%.

The NM (Pt, Pd, Ag, Au)–GT ternary composites exhibited the evidenced enhancement of the photocatalytic activity under visible light irradiation compared to the undoped GT hybrid support. The formation of heterostructures played the key role in the highly efficient photocatalytic performance. The presence of a metal at the surface of TiO2 would result in the formation of a Schottky barriers at the metal-semiconductor surface. As the Fermi levels of Pt, Pd, Ag and Au were lower than that of TiO2, photoexcited electrons were transferred from the conducton band of TiO2 to the metal particles, while the photogenerated valence band holes remained on TiO2. Therefore the photocatalytic activity was improved owing to the longer electron–hole pair separation life time.

4. Conclusion

We have presented a review of recent experimental research on improving the photocatalytic activity of TiO2 by combining TiO2 NPs with nanocarbons of different types. Beside SWCNT and MWCNT, G and GO were efficiently utilized. In particular, the research on the improved photocatalytic activity of nanocomposites comprising TiO2 NPs and G or GO, and also NPs of noble metals and metallic oxides, has been rapidly developed in last years and proved a very promising trend in the research on photocatalysis.

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References

[1] Barni B et al 1995 Chemosphere 30 1861
[2] Gianturco F et al 1996 Chemosphere 33 1531
[3] Bario O, Gawlik B M, Bellobono I R and Muntau H 1998 Chemosphere 37 975
[4] Hermann J M et al 1999 Catalysts Today 54 353
[5] Ahmed S, Rasul M G, Martens W N, Brown R and Hashish M A 2010 Desalination 261 3
[6] Miguel N, Ormad M P, Mosteo R and Oveilleiro J L 2012 Int. J. Photoenergy 2012 371714
[7] Zhu X-D, Wang Y-J, Sun R-J and Zhou D-M 2013 Chemosphere 92 925
[8] Diao Z, Li M, Zeng F, Song L and Qiu R 2013 Journal of Hazardous Materials 260 585
[9] Nguyen V H and Nguyen B H 2012 Adv. Nat. Sci.: Nanosci. Nanotechnol. 3 023001
[10] Subramanian V, Wolf E E and Kamat P V 2004 JACS 126 4943
[11] Tian Y and Tatsuma T 2005 JACS 127 7632
[12] Hirakawa T and Kamat P V 2005 JACS 127 3928
[13] Awazu K, Fujimaki M, Rockstuhl C, Tomitazaza J, Murakami H, Ohki Y, Yoshida N and Watanabe T 2008 JACS 130 1676
[14] Xiang Q, Ju J and Jaroniec M 2012 Chem. Soc. Rev. 41 782
[15] Wang W, Serp P, Kalck P and Faria J L 2005 Appl. Catal. B: Environmental 56 305
[16] Yao Y, Li G, Ciston S, Lueptow R M and Gray K A 2008 Environ. Sci. Technol. 42 4952
[17] Gao B, Peng C, Chen G Z and Li Puma G 2008 Appl. Catal. B: Environmental 85 17
[18] Li Z, Gao B, Chen G Z, Mokaya R, Sotiropoulos S and Li Puma G 2011 Adv. Nat. Sci.: Nanosci. Nanotechnol. 6 (2015) 033001 Review