Nanostructured hybrid materials based on reduced graphene oxide for solar energy conversion

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ABSTRACT

Research on carbon-based photocatalytic nanomaterials has been a field in continuous expansion in the last years. Graphene (or its derivatives) is currently one of the most studied materials due to its high surface area, photodegradation resistance, optical transparency and high charge mobility values. All of these excellent properties are highlighted for applications in various research areas. The incorporation of small amounts of reduced graphene oxide (RGO) sheets in semiconductors matrices is also a strategy widely used to improve the physicochemical properties, which cannot normally be achieved using conventional composites or pristine semiconductors. Most studies suggest that these two-dimensional (2D) materials can facilitate electron injection and assist the electron transport in semiconductors. In this context, this manuscript will present examples of graphene-based semiconductor nanocomposites obtained by our research group and their application in the photodegradation of methylene blue (MB), photocatalytic conversion of CO_2 to hydrocarbon fuels and photocatalytic water splitting reaction. Our results show the positive effect of coupling the RGO sheets with semiconductors for photocatalysis.

Keywords: reduced graphene oxide, nanocomposites, photocatalysis, CO_2 photoreduction, water splitting

1 INTRODUCTION

The nanomaterials, whose particle sizes are in the nanometer range (1 nm = 10^{-9} m), have aroused great interest in the scientific community because of their unusual physicochemical properties influenced by the surface effect and quantum size effect. The use of these properties in technological applications forms the basis of the nanotechnology for making advanced materials. Fullerenes, carbon nanotubes and graphene sheets are some of the attractive options because these materials are constituted essentially by carbon, which is a versatile chemical element to form single, double and triple bonds with other atoms. This element is present in the nature in several allotropic forms and it is capable of forming various chemical compounds.[1, 2] A brief review of the literature involving carbon-based nanomaterials shows a fast growth for applications in electronic, optoelectronic and photovoltaic devices. The proper combination of these materials also enables their application in photocatalytic systems for several reactions.[1, 3-10]

Photocatalysts are widely used to remove organic pollutants or harmful compounds and to split water into oxygen (O_2) and hydrogen (H_2) gas.[11, 12] Photocatalytic carbon dioxide (CO_2) reduction is also another strategy employed to transform harmful greenhouse gases (such as CO_2) into valuable solar fuels, such as methane (CH_4) and methanol (CH_3OH).[13] All these applications are based on the use of solar energy, which is a clean, cheap, safe and inexhaustible source. In general, photocatalysts play a major role in curbing serious environmental and pollution challenges. There are some requirements for a given material to act as a photocatalyst. These materials must present band edge potentials appropriate for redox reaction of the species of interest and suitable solar visible-light absorption capacity. Efficient charge separation and charge transport are desired to avoid the unwanted recombination processes. A good stability in aqueous environment, resistance to photocorrosion, non-toxicity, environmentally friendly and low cost are also important characteristics for the photocatalyst. However, each photocatalyst has its own limitations. Research strategies have been primarily focused on addressing these limitations and achieving better photocatalyst performance.

Research on carbon-based photocatalytic nanomaterials has been a field in continuous expansion in the recent years. Carbon materials, especially carbon nanotubes (CNTs), quantum dots, carbon fibers and activated carbon are frequently applied as supporting materials to anchor small semiconductor nanostructures.[9] Another carbonaceous material that has been widely used for this application is graphene or its derivatives.

Firstly, graphene is the name given to a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice.[14] This material has attracted attention from the scientific community because of its high mobility values that can exceed 200 000 cm^2 V^{-1} s^{-1} at low temperatures.[15] Other more remarkable properties of graphene are large theoretical specific surface area (2630 m^2 g^{-1})[16], high Young's modulus (*ca.* 1.0 TPa)[17], excellent thermal conductivity (*ca.* 5000 W m^{-1} K^{-1})[18] and optical transparency (*ca.* 97.7%)[19]. All of these properties are highlighted for applications in field-effect transistors[20, 21], chemical and biological sensors[22], energy storage[23], drug delivery[24], batteries[25], supercapacitors[26], transparent conductive films[27], light-emitting diodes[28], photovoltaic devices[29,30], photocatalysts[11,13] and so on. It is also noteworthy that its hexagonal network forms a basic building block for other carbon allotropes, such as graphite, nanotubes and fullerenes. In fact, most of the electronic and structural properties of these allotropes can be derived from the basic properties of graphene.[2, 14, 31]

Graphene oxide (GO), a graphene derivative, is an electrically insulating material and usually exhibits a rich assortment of oxygen-containing groups such as carboxylic, hydroxyl, carbonyl, and epoxide groups (Fig. 1(a)). The presence of these oxygen-containing groups on the surface of GO facilitates the preparation of graphene-based nanoarchitectures or nanocomposites in aqueous solutions. These functional groups are also excellent reactive sites for a variety of functionalization reactions or nucleation and growth of nanoparticles.[32, 33] The electrical conductivity of GO can be increased by reduction and partial restoration of the sp^2 hybridized network. The resulting product, also known as reduced graphene oxide (RGO) have a wrinkled, soft and disordered morphology in the powder form, as shown in Fig. 1(b).[34] These wrinkles can cause deviation from the sp^2/planar character expected for graphene monolayer. The presence of vacancies, heptagon and pentagon rings, edge effects and functional groups are also some of the factors that contribute to the formation of defects in the structure.[35, 36] The RGO sheets have properties which are similar to graphene, although the reduction methods do not fully restore the ideal characteristics of graphene sheets.
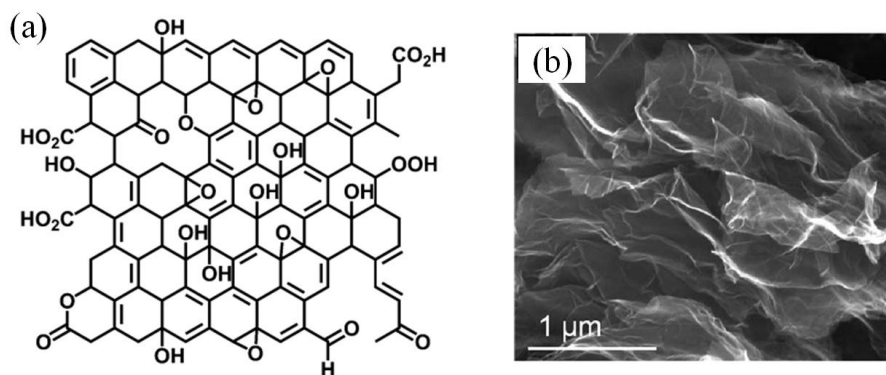

Figure 1. (a) Structural model of graphene oxide (GO) proposed by Lerf-Klinowski (Reprinted with permission from ref.[37]. Copyright 2012, Royal Society of Chemistry. (b) Field emission scanning electron microscope (FEG-SEM) image of wrinkled graphene obtained from graphene oxide (GO) sheets (Reprinted with permission from ref. [34]. Copyright 2012, American Institute of Physics).

A great number of semiconductor nanostructures have been combined with graphene (or its derivatives), which include oxides such as TiO$_2$[38], ZnO[39], α-Fe$_2$O$_3$[40], Fe$_3$O$_4$[41], NiO[42], SnO$_2$[43], Co$_3$O$_4$[44], Cu$_2$O[45], WO$_3$[46] and other semiconductors such as CdS[47], ZnS[48], CdSe[49], BiVO$_4$[50], MoS$_2$[51] and g-C$_3$N$_4$[52]. Although the advantages of the incorporation of graphene-like sheets in semiconductor matrices for application in photocatalysis are well known, unfortunately, a detailed understanding of the role of these carbonaceous materials is still very controversial in the literature. Some studies have reported an improvement in the interaction between the graphene-based photocatalysts and the organic compounds. One of the first works, Zhang *et al.*[53] demonstrated that the increase of reduced graphene oxide (RGO) concentration in the TiO$_2$/RGO nanocomposites promotes an increase in the adsorption of methylene blue, due to favorable π-π interactions between the organic dye and the RGO sheets. It is noteworthy that the surface adsorption is a prerequisite for photocatalytic processes. Many reports also show that graphene (or its derivatives) is able to extend the light absorption range of semiconductors. In this case, the surface carbon doping effect could lead to a band-gap narrowing of the semiconductor because of the chemical bonding between semiconductor and graphene.[54, 55] Other studies have demonstrated that graphene can act as a sensitizer in semiconductor oxide films.[56, 57] Zhang *et al.*[56] were the first to propose a photocatalytic mechanism where the role of the RGO sheets in the ZnS-RGO nanocomposites acts as an organic dye-like macromolecular "photosensitizer" for ZnS. Most studies suggest that these carbon-based materials can facilitate electron injection and assist in electron transport.[58] Ng *et al.*[59] reported that the TiO$_2$(P25)-RGO
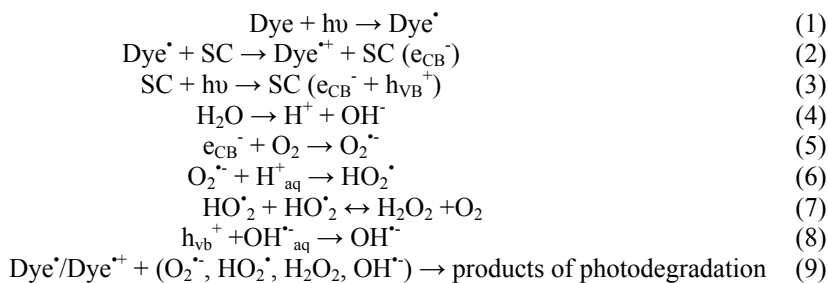
nanocomposite electrodes showed significant activity for photocatalytic decomposition of 2,4-dichlorophenoxyacetic acid. According to the researchers, the RGO sheets can create a 2D conductive support path for charge transport and collection at the electrode surface. In summary, there is also a need for a more detailed investigation of the role of graphene (or its derivatives) sheets in the semiconductor matrices, and how this successful combination of materials has improved the photocatalytic performance of several oxides. In this context, we will present some graphene-based semiconductor nanocomposites obtained by our research group and their application in photocatalysis for photodegradation of methylene blue (MB), photocatalytic conversion of CO_2 to hydrocarbon fuels and photocatalytic water splitting reaction.

2 APPLICATION OF GRAPHENE-BASED SEMICONDUCTOR PHOTOCATALYSTS

2.1 Photodegradation of methylene blue (MB)

The environmental pollution is a consequence of the rapid development of modern industry, which threatens human health. Hence, the pollutant elimination has become one of the most important research fields.[60] The photocatalytic degradation of organic pollutants into harmless end products has become a promising green route, based on the global energy crisis, sustainability and renewability of solar light.[61] Among the many dyes used in the industries, the most common is the methylene blue (MB) because it is widely used from printing fabrics and its residues are difficult to treat by conventional methods due to its strong interaction with a large variety of substrates.[62] MB is also employed as dye model to investigate the performance of new photocatalysts. Therefore, the degradation of this dye and all organic pollutants must be performed by the direct ultraviolet light or sunlight in the presence of a semiconductor (SC), acting as a catalyst of the process.[63]

The mechanism follows the production of hydroxyl radicals, which are able to oxidize and mineralize almost any organic molecule, yielding CO_2, H_2O and inorganic ions (reactions shown below). The photocatalytic reaction is initiated by the generation of an electron and hole pair upon semiconductor photoirradiation, where electrons are ejected from the valence band of the semiconductor (Eq. 3). These electrons generate intermediate superoxide radicals ($O_2^{\bullet-}$) by reacting with chemisorbed oxygen on catalyst surface (Eq. 5), which along with H^+, form hydroperoxyl radicals ($\bullet HO_2$) (Eq. 6), subsequently producing H_2O_2 (Eq.7). The hydrodyl radicals are formed by the reaction with holes (h^+) with adsorbed water (OH_2) on the catalyst surface (Eqs. 4 and 8). The photodegradation of the MB into non-toxic organic compounds is performed by the reaction between the dye and the formed reactive radicals.[63]

$$Dye + h\upsilon \rightarrow Dye^{\bullet} \tag{1}$$
$$Dye^{\bullet} + SC \rightarrow Dye^{\bullet +} + SC\ (e_{CB}^{-}) \tag{2}$$
$$SC + h\upsilon \rightarrow SC\ (e_{CB}^{-} + h_{VB}^{+}) \tag{3}$$
$$H_2O \rightarrow H^+ + OH^- \tag{4}$$
$$e_{CB}^{-} + O_2 \rightarrow O_2^{\bullet-} \tag{5}$$
$$O_2^{\bullet-} + H^+_{aq} \rightarrow HO_2^{\bullet} \tag{6}$$
$$HO^{\bullet}_2 + HO^{\bullet}_2 \leftrightarrow H_2O_2 + O_2 \tag{7}$$
$$h_{vb}^{+} + OH^{\bullet-}_{aq} \rightarrow OH^{\bullet-} \tag{8}$$
$$Dye^{\bullet}/Dye^{\bullet +} + (O_2^{\bullet-}, HO_2^{\bullet}, H_2O_2, OH^{\bullet-}) \rightarrow products\ of\ photodegradation \tag{9}$$

Titanium dioxide or titania (TiO_2) is well-known and the most investigated among the semiconductors for photocatalysis, due to its low cost and better chemical and optical stability.[53, 64] With a bandgap of 3.2 eV, this semiconductor can only be excited by ultra-violet (UV) irradiation, corresponding just 4 % of the solar energy reaching the Earth.[65] Besides, TiO_2 exhibits high recombination rate of the photogenerated electron-hole pairs, which aroused the interest of many researchers to overcome such limitations, attempting to shift the light absorption towards visible light and to increase the lifetime of the photogenerated electrons and hole pairs.[62]

Our group reported recently[62] the synthesis and characterization of a nanocomposite composed based on titanium dioxide (TiO_2), cuprous oxide (Cu_2O) nanoparticles and reduced graphene oxide (RGO) sheets. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Fig. 2(a-b)) showed that the TiO_2 and Cu_2O nanoparticles are uniformly distributed across the surface of the RGO sheets. The photocatalytic activity of the $TiO_2/Cu_2O/RGO$ nanocomposite, the precursors (TiO_2 and Cu_2O) and the intermediate nanocomposites (TiO_2/RGO and Cu_2O/RGO) were studied through the photodegradation of MB under solar radiation. The graph in Fig. 2(c) shows the relative variation in the absorbance of the MB solution over time under the influence of the synthesized photocatalysts under solar light illumination. In this work, a considerable increase in the photodegradation activity using the ternary

nanocomposite was obtained after 5 h ($\sim$ 95 % of MB degradation). Photoelectrochemical studies were also carried out and the results showed an enhancement in the anodic photocurrent values for the ternary nanocomposite, corroborating with the photocatalytic data. The positive effect of the RGO sheets is due to their ability to accept and transfer electrons from semiconductors. Coupling two semiconductors (TiO_2 and Cu_2O) with complementary absorption profiles and suitable energy levels was also decisive for the improvement of the photocatalytic and photoelectrochemical results with the use of the ternary nanocomposite.
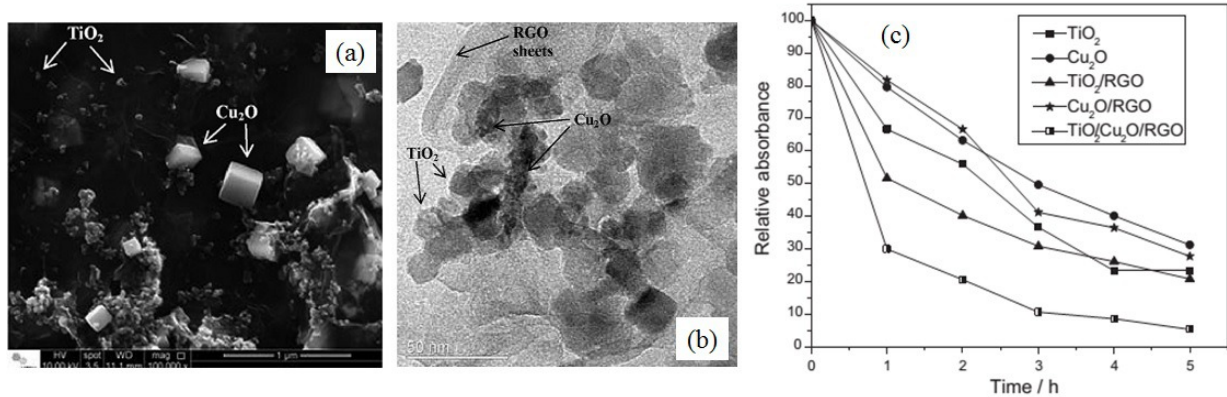

Figure 2. (a) SEM and (b) TEM images of the $TiO_2/Cu_2O/RGO$ nanocomposite. (c) Relative optical absorbance of the methylene blue solutions during the photodecomposition tests on TiO_2, Cu_2O, TiO_2/RGO, Cu_2O/RGO and $TiO_2/Cu_2O/RGO$. Reprinted with permission from ref. [62]. Copyright 2015, Elsevier.

Hematite (α-Fe_2O_3) is one of the most promising candidates for photocatalytic application, due to its narrow band gap of 2.0-2.2 eV, making it possible to absorb light up to 600 nm, which corresponds to almost 40 % of the solar spectrum. This semiconductor is stable in most aqueous solutions and is one of the cheapest semiconductor materials available.[63] Although, the hole diffusion length of hematite is much smaller ($\sim$ 4 nm) than the width of the space-charge layer, the incorporation of rGO in the hematite can overcome such limitations due to graphene's exceptional properties.[66]

Pristine hematite nanoparticles and hematite/rGO nanocomposites with different amounts of rGO were used for photodegradation of MB. The composites were synthesized by hydrothermal method and the concentration of rGO in the composites was 4.5 and 7.0 wt %. The reactions were conducted in a solar simulator (AM1.5G conditions), in which aliquotes were collected to measure the absorption of MB over time. Fig 3(a-b) shows the FEG-SEM images of α-Fe_2O_3-rGO nanocomposites, showing the rGO nanosheets wrapping the α-Fe_2O_3 nanoparticles. The good interaction between them is necessary to allow the electron transport through the rGO sheets. The results showed a better performance by the nanocomposites, when compared with the pristine α-Fe_2O_3, reaching almost 70 % of photodegradation. We ascribe this performance due to the presence of rGO sheets that are able to collect and transport electrons across their 2D network towards the target site for dye degradation.
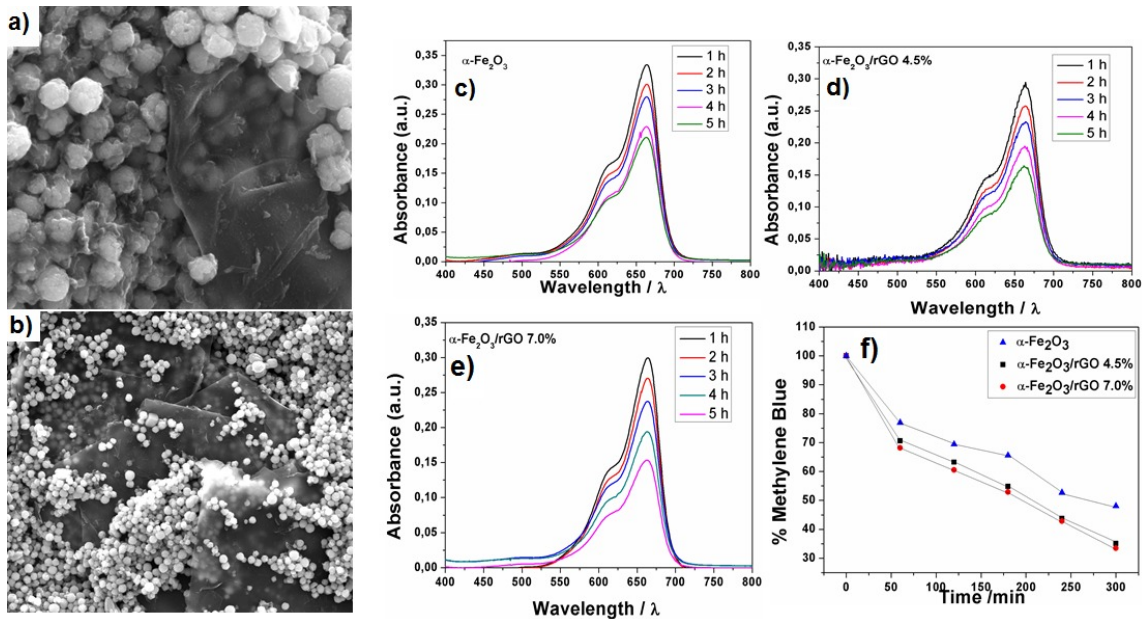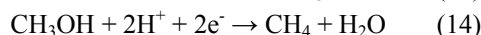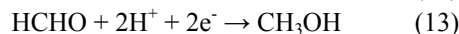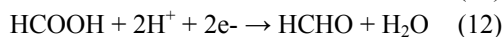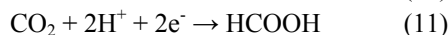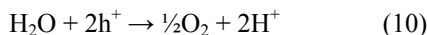
Figure 3. (a) (b) FEG-SEM images of α-Fe$_2$O$_3$/rGO nanocomposites. UV-Vis spectra of methylene blue after 5 hours of photodegradation by (c) pristine α-Fe$_2$O$_3$, (d) α-Fe$_2$O$_3$/rGO 4.5%, (e) α-Fe$_2$O$_3$/rGO 7.0% and (f) methylene blue concentration over time.

2.2 Photocatalytic conversion of CO$_2$ to hydrocarbon fuels

Carbon dioxide (CO$_2$) is one of the main greenhouse gases, which contributes largely to the global climate change. The conversion of CO$_2$ into hydrocarbons appears to be a promising alternative to reduce emissions of this gas in the atmosphere. In 1979, Inoue *et al*.[67] reported for the first time the photoelectrocatalytic CO$_2$ reduction into organic compounds, such as formic acid (HCO$_2$H), formaldehyde (HCHO), methanol (CH$_3$OH) and methane (CH$_4$), using a variety of semiconductors powders suspended in CO$_2$-saturated water illuminated by a Xe lamp. Since then, many studies have been carried out using various types of semiconductors with different compositions and morphologies.[68] According to Inoue *et al*.[67], the conversion of CO$_2$ to methane involves a multistep reduction process given by:

$$H_2O + 2h^+ \rightarrow \tfrac{1}{2}O_2 + 2H^+ \qquad (10)$$
$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad (11)$$
$$HCOOH + 2H^+ + 2e- \rightarrow HCHO + H_2O \qquad (12)$$
$$HCHO + 2H^+ + 2e^- \rightarrow CH_3OH \qquad (13)$$
$$CH_3OH + 2H^+ + 2e^- \rightarrow CH_4 + H_2O \qquad (14)$$

where e$^-$ and h$^+$ denote photogenerated electrons and holes, respectively. First, the presence of h$^+$ promotes water splitting, resulting in the formation of oxygen gas (O$_2$) and H$^+$ ions. These H$^+$ ions, when combined with CO$_2$ molecules and e$^-$, promote the formation of organic molecules (hydrocarbons), which at the end of the process are converted to CH$_4$ by adding more H$^+$ and e$^-$.[69]

TiO$_2$ is again the most studied semiconductor as a photocatalyst due to the properties already discussed previously. In this context, graphene-based TiO$_2$ photocatalysts have also been widely used in CO$_2$ photoreduction.[70, 71] The photoactivity of this semiconductor is only observed when it is irradiated with ultraviolet light, which corresponds approximately to 5 % of incident solar energy. This drawback can be circumvented by doping TiO$_2$ with anions or cations[29, 72], by its sensitization with dyes[73] or by combining with another semiconductor with a narrow band gap that is able to absorb radiation within the visible range[74]. Cadmium sulfite (CdS) has been widely used in conjunction with TiO$_2$ in photocatalytic systems due to its strong absorption in the visible region and because its conduction band relies above that of the TiO$_2$. The use of TiO$_2$/CdS composites provide optical and catalytic properties that differ from those of the individual constituent materials[74, 75].

The photogenerated electrons in the semiconductor (no potential application to the system) are conducted through the material by diffusion, usually among the nanoparticles. This electron diffusion is not efficient and leads to an increase of charge recombination processes, reducing the photocatalytic efficiency.[76] An interesting alternative to reduce this effect is the incorporation of carbon-based materials into semiconductor matrices.[77-81] Graphene and its derivatives have been often used in photocatalytic CO_2 reduction process.[13, 82] The combination of TiO_2 nanoparticles and RGO sheets remains a good strategy to improve the photocatalytic performance of semiconductor oxides for several reactions. The electron-accepting ability presented by the RGO sheets can be used to enhance the electron transport properties of the TiO_2 films.[59, 83] The metal nanoparticles (Au, Ag, Cu, Ni, Ti, Co, Rh, Ir, Pt and so on) commonly used as co-catalysts is also a strategy to improve the performance of the TiO_2 photocatalyst. Small amounts these co-catalysts are usually deposited onto the semiconductor surface or onto the surface of carbonaceous materials. Platinum (Pt) is the most widely used metal as co-catalyst because of its stability, chemical inertness and high catalytic activity.[84]

In this context, in 2015, our research group[85] reported the use of the quaternary $TiO_2/CdS/rGO/Pt$ nanocomposite as a catalyst for the photocatalytic reduction of CO_2 to CH_4, using water and visible light as energy sources. Samples of TiO_2/CdS and rGO/Pt were prepared separately and then mixed to obtain $TiO_2/CdS/rGO/Pt$ nanocomposite films. The synthesized materials were characterized through X-ray diffraction (XRD), Raman spectroscopy, UV-vis spectroscopy, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) images. The XRD data of the $TiO_2/CdS/rGO/Pt$ sample indicated that anatase was the main crystalline phase in pristine TiO_2, likely due to the simultaneous synthesis of CdS in conjunction with TiO_2. The SEM image (Fig. 4(a)) showed that the TiO_2/CdS and Pt nanoparticles have a large dispersion over the entire rGO sheet. The mapping of the elements (EDS analysis) also confirmed the presence of all components distributed over the RGO sheets in an intimate contact, which is important for the success of the photocatalytic reaction (Fig. 4(b-g)).
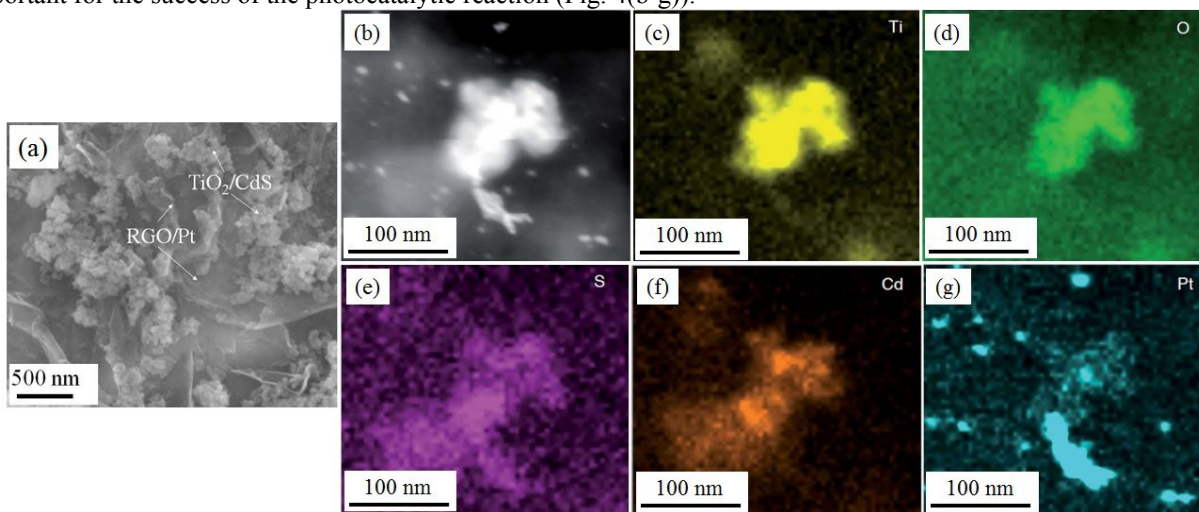

Figure 4. (a) SEM image of the $TiO_2/CdS/rGO/Pt$ quaternary nanocomposite. EDS analyses of $TiO_2/CdS/Pt$ nanoparticles on reduced graphene oxide (rGO): (b) high angle annular dark field (HHADF) image, (c) titanium map, (d) oxygen map, (e) sulfur map, (f) cadmium map and (g) platinum map. Reprinted with permission from ref.[85]. Copyright 2015, Royal Society of Chemistry.

The photocatalytic activity of the materials was investigated for 5 h under AM 1.5 illumination. After this period, 0.11 μmol of CH_4 was produced at an average production rate of 0.0867 μmol h^{-1}, which is higher than the production of CH_4 measured from the TiO_2, TiO_2/CdS and the $TiO_2/CdS/Pt$ control samples (Fig. 5(a)). This effect results from the beneficial synergy between all the four components in the photogeneration, charge separation and transport of the charge carriers. The enhanced electron transport in the $TiO_2/CdS/rGO/Pt$ nanocomposite films was also evidenced in the photoelectrochemical measurements (Fig. 5(b)).[85]
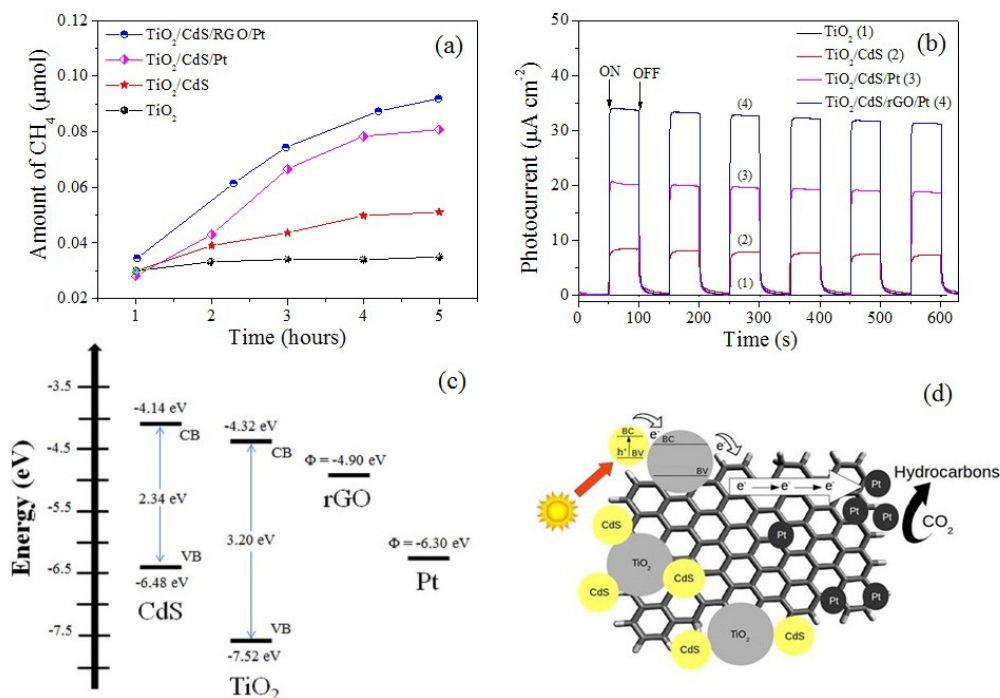
Figure 5. (a) Amount of methane produced by the photocatalysis reaction in the presence of water and carbon dioxide for the samples: TiO_2, TiO_2/CdS, $TiO_2/CdS/Pt$ and $TiO_2/CdS/rGO/Pt$. Reaction parameters: 50 mg of photocatalyst, CO_2 pressure inside the reactor equal to 0.2 bar, 0.5 mL of water, and illumination (100 mW cm^{-2}) for 5 h. (b) Time-dependent photocurrent density (chronoamperometry) at 0 V versus Ag/AgCl applied bias potential in an aqueous electrolyte containing 1 mol L^{-1} Na_2SO_3 and using the TiO_2 (1), TiO_2/CdS (2), $TiO_2/CdS/Pt$ (3) and $TiO_2/CdS/rGO/Pt$ (4) films on an FTO substrate as the working electrode. (c) Energy level diagrams for TiO_2, CdS, rGO and Pt. (d) Schematic illustration of the photoinduced charge separation and transfer process in the nanocomposite. Reprinted with permission from ref. [85]. Copyright 2015, Royal Society of Chemistry.

The relative energetic positions of the conduction band (CB), valence band (VB) and work function (Φ) for TiO_2, CdS, rGO and Pt are shown in Fig. 5(c). A schematic illustration of the photoinduced charge separation and transfer process in the $TiO_2/CdS/rGO/Pt$ quaternary nanocomposite is presented in Fig. 5(d). It is difficult to quantitatively evaluate the contribution of each component separately. When the $TiO_2/CdS/rGO/Pt$ nanocomposite is exposed to visible light, excited electron–hole pairs are generated in both semiconductors. Due to the specific nature of the band alignment at the TiO_2/CdS interface, the photogenerated electrons are transferred to the CB of TiO_2, whereas the holes remain in the VB of CdS. We strongly believe that the electrons are transported more efficiently through the rGO sheets, decreasing the recombination between electrons in the CB of TiO_2 and holes in the VB of CdS. The rGO sheets are a well-known electron-accepting material with excellent conductivity properties as a result of its two-dimensional planar structure. In addition, the presence of Pt nanoparticles as co-catalyst also efficiently contributes to conduct electrons towards CO_2 molecules, thereby reducing them to CH_4. The combination of the potential advantages of each component resulted in an increase in light absorption, in a decrease in the charge recombination processes and it also facilitated the electron transfer across the heterojunction interfaces.

2.3 Photocatalytic water splitting

Since Fujishima and Honda[86] (1972) published the first report on photoelectrochemical splitting of water into hydrogen (H_2) and oxygen (O_2) over titanium dioxide (TiO_2) photoanodes, different types of semiconductors have been developed and evaluated as potential candidates for solar-driven hydrogen production.[87] The efficient conversion of solar energy to produce hydrogen via photoelectrochemical cells (PEC) to split water molecules has been regarded as a promising alternative for sustainable, future power generation. Iron oxide in the hematite phase (α-Fe_2O_3) has many

advantages to be used in a PEC as already mentioned early. As described in item 2.1, the incorporation of rGO in the hematite can overcome some inherent drawbacks, as small hole diffusion length in the α-Fe_2O_3.[88]

We have recently reported[88] an effective method to prepare reduced graphene oxide (rGO)/Fe_2O_3 nanostructured photoanodes. Photoelectrochemical characterization towards water splitting reactions was conducted as shown in Fig. 6. First, graphene oxide (GO) is reduced into rGO using hydrazine, and then deposited over the nanostructured hematite photoanodes previously treated at 750 ºC for 30 min. The pristine hematite photoanode and the hematite photoanode modified with reduced graphene oxide were called F1 and F1/rGO, respectively. Other two photoelectrodes with different hematite nanoparticles sizes were also tested (F2 and F3, with particles size of 450 nm and 640 nm, respectively). Using our strategy, the rGO incorporation results in a photocurrent density increase from 0.56 to 0.82 mA cm^{-2} at 1.23 V_{RHE} for the F1/rGO photoanode that compromises hematite nanoparticles of ~200 nm. Our results indicate that the rGO incorporation on the hematite photoanodes shows a positive effect in the reduction of electron–hole recombination rate. This method was effective to enhance the efficiency of the water splitting process under sunlight illumination. The enhancement in photocurrent was attributed to the reduction of the electron–hole recombination process and an improved hole transfer to the electrolyte/electrode interface in the presence of rGO.
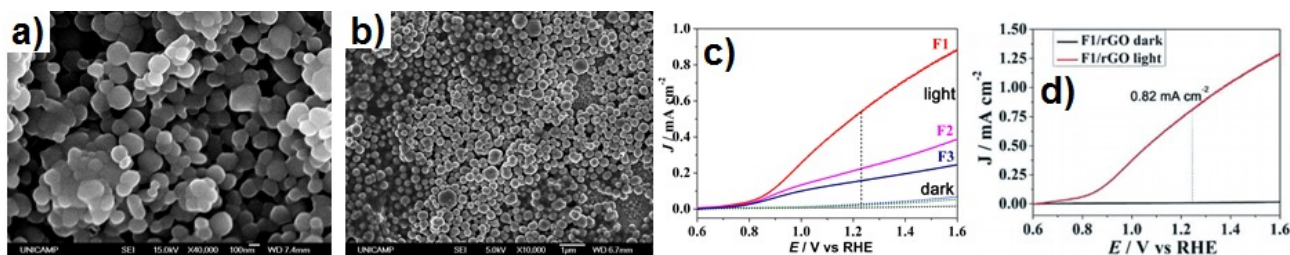

Figure 6. (a) Top-view SEM images of the pristine hematite photoanode film (F1) and (b) the modified film with reduced graphene oxide layers deposited by drop-casting on its surface (F1/rGO). Potential (V_{RHE}) vs. photocurrent density (mAcm^{-2}) of (c) the pristine hematite photoanode and (d) F1 modified with reduced graphene oxide. Reprinted with permission from ref.[88]. Copyright 2016, Wiley Online Library.

Although several reports in the literature have explored the benefits of RGO addition in titania films for photocatalysis and water splitting reactions, the role of RGO in the composite is always described as that of a material that is able to act as an electron acceptor and transport electrons more efficiently. However, in most of these reports, no clear evidence for this ''role'' is presented, and the main focus is deviated to the improved efficiency and not to the fundamental reasons. In a recent work, we employed several techniques to definitively present our understanding of the role of RGO in titania composite films.[89] Nanocrystalline TiO_2 and reduced graphene oxide (TiO_2/RGO) composite films were prepared by combining a sol-gel method with hydrothermal treatment, employing titanium isopropoxide ($Ti(O^iPr)_4$) and graphene oxide (GO) as starting materials. For the TiO_2/RGO composites, HRTEM image showed that the RGO sheets are completely covered and decorated with TiO_2 nanoparticle (Fig. 7(a)). This strong interaction between the RGO sheets and the TiO_2 nanoparticles is important to achieve a good electronic coupling between these two materials.
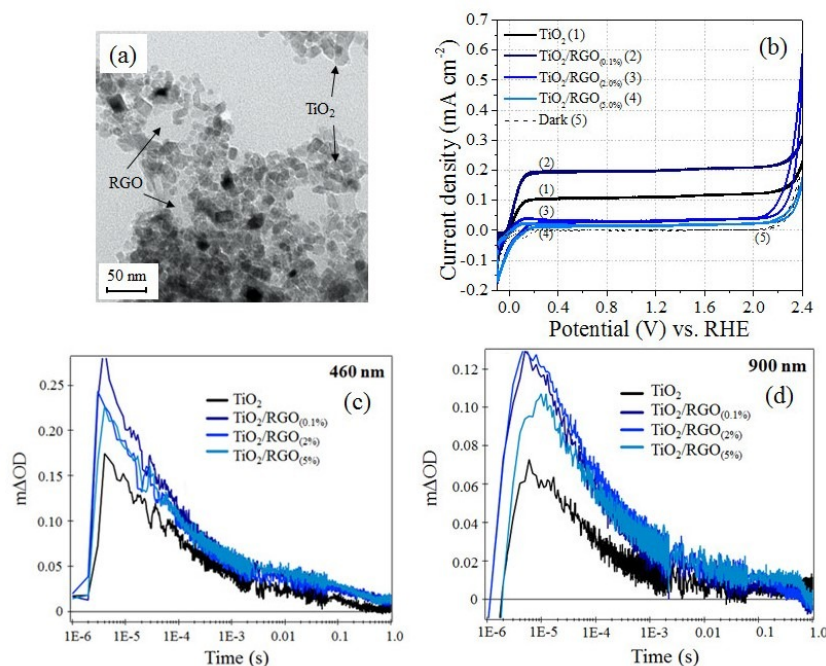
Figure 7. (a) HRTEM image of the $TiO_2/RGO_{(5\%)}$ nanocomposite. (b) Cyclic voltammograms obtained using the TiO_2, $TiO_2/RGO_{(0.1\%)}$, $TiO_2/RGO_{(2\%)}$ and $TiO_2/RGO_{(5\%)}$ films as photoanodes in 0.5 mol L^{-1} H_2SO_4, in the dark and under illumination. Transient absorption spectra of (c) photoholes (460 nm) and (d) photoelectrons (900 nm) in the same films after Nd:YAG laser excitation, in the ultraviolet region (355 nm), in nitrogen atmosphere and in the absence of chemical scavengers. Reprinted with permission from ref. [89]. Copyright 2016, Royal Society of Chemistry.

The influence of the addition of different amounts of RGO to the TiO_2 matrix was investigated in the photoelectrochemical water splitting studies. The $TiO_2/RGO_{(0.1\%)}$ photoelectrodes showed the highest photocurrent density values (0.20 mA cm^{-2} at 1.23 V_{RHE}) compared to other electrodes, with an increase of 78 % in relation to pristine TiO_2 film (0.11 mA cm^{-2} at 1.23 V_{RHE}), as shown in Fig. 7(b). The sensitization effect of RGO in the titania film was not observed in our study. Moreover, the energy levels of both materials do not allow charge transfer from the RGO to the titania conduction band. However, the opposite can be accomplished. In this work, transient absorption spectroscopy (TAS) was also employed to correlate the excited state dynamics with the electrochemical reactions at the photoanode (Fig. 7(c-d)). In all the nanocomposite films containing RGO sheets, we observed an increase in the amplitude of the long lived 460 nm (photohole) and 900 nm (photoelectron) signals in comparison with the TiO_2 film.

According to Meng *et al.*[90], who also used TAS as an additional tool to understand the photocatalytic improvement of TiO_2/α-Fe_2O_3 composite for water oxidation, the mechanism is associated with mobile electrons, which are initially created in semiconductors and quickly transfer to the RGO sheet, wherein they diffuse into trap states in the RGO on a time scale of picoseconds. The optical density variation (ΔOD) observed is proportional to the number of charge carriers photogenerated and this is a strong indication of a decrease in the charge recombination.

We also observed a correlation between the TAS results and the photoelectrochemical studies.[89] The sample that gave rise to the best performance in the water oxidation process ($TiO_2/RGO_{(0.1\%)}$) also originated the highest yield for both charge carriers. However, at higher concentrations (0.5 to 5.0 wt%), the photocurrent density values sharply decrease, probably due to the darkening and the agglomerations of RGO sheets in these films, which deteriorated the electrical parameters. We propose that in films with lower concentrations ($\leq$ 0.1 wt%), the positive effect of the RGO sheets is due to their ability to accept and transfer electrons from TiO_2. The immediate consequence is a decrease in charge recombination, observed by the increase in the photogeneration of holes and electrons in TAS decays and a significant improvement in the photocurrent density in photoelectrochemical water splitting.

3   SUMMARY AND PERSPECTIVES

The various areas of research based on the use of graphene (or its derivatives) have grown fast since the first work by Novoselov *et al.*[91]. The unique properties of these two-dimensional (2D) materials in combination with the extremely rich chemistry of the carbon element allow their applications in photocatalytic systems. In this manuscript, we higligted the graphene-based semiconductor nanocomposites obtained by our research group and their application in photocatalysis for photodegradation of MB, reduction of CO_2 and water splitting reaction. The strong interaction between the RGO sheets and the semiconductor nanoparticles proved to be very important to achieve a good electronic coupling between these two materials. However, due to their high complexity, the future works must first focus on developing simple and efficient preparation methods for these nanocomposites. The challenge is to develop new preparation methods in order to obtain high quality RGO sheets and with control over the number of layers. The development of new architectures (nanotubes, nanowires, nanofibers, nanobelts, nanosheets and nanorods) is also one of the alternatives to improve the performance of semiconductors by increasing the semiconductor surface area and/or electronic transport. The use of transient absorption techniques is also a powerful tool to clear understand the RGO behavior, especially about the dynamics of electrons and holes. On the other hand, the great number of applications and property-oriented possibilities suggests that future research and prospects for graphene-based semiconductors are likely to expand in any research field.

4   ACKNOWLEDGEMENT

5   REFERENCES

[1] Jariwala, D., Sangwan, V. K., Lauhon, L. J., Marks, T. J. and Hersam, M. C., "Carbon nanomaterials for electronics, optoelectronics, photovoltaics, and sensing", Chem Soc Rev, 42, 2824-2860 (2013).

[2] Geim, A. K. and Kim, P., "Carbon wonderland", Sci Am, 298, 90-97 (2008).

[3] An, X. Q. and Yu, J. C., "Graphene-based photocatalytic composites", Rsc Adv, 1, 1426-1434 (2011).

[4] Singh, V., Joung, D., Zhai, L., Das, S., Khondaker, S. I. and Seal, S., "Graphene based materials: Past, present and future", Progress in Materials Science, 56, 1178-1271 (2011).

[5] Sun, Y., Wu, Q. and Shi, G., "Graphene based new energy materials", Energ Environ Sci, 4, 1113-1132 (2011).

[6] Xiang, Q. J., Yu, J. G. and Jaroniec, M., "Graphene-based semiconductor photocatalysts", Chem Soc Rev, 41, 782-796 (2012).

[7] Zhang, N., Zhang, Y. H. and Xu, Y. J., "Recent progress on graphene-based photocatalysts: current status and future perspectives", Nanoscale, 4, 5792-5813 (2012).

[8] Su, D. S. and Centi, G., "A perspective on carbon materials for future energy application", J Energy Chem, 22, 151-173 (2013).

[9] Cao, S. and Yu, J., "Carbon-based H_2 production photocatalytic materials", Journal of Photochemistry and Photobiology C: Photochemistry Reviews, 27, 72-99 (2016).

[10] Yang, Y., Han, C., Jiang, B., Iocozzia, J., He, C., Shi, D., Jiang, T. and Lin, Z., "Graphene-based materials with tailored nanostructures for energy conversion and storage", Materials Science and Engineering R, 102, 1-72 (2016).

[11] Xiang, Q. and Yu, J., "Graphene-Based Photocatalysts for Hydrogen Generation", J Phys Chem Lett, 4, 753-759 (2013).

[12] Zhang, N., Yang, M.-Q., Liu, S., Sun, Y. and Xu, Y.-J., "Waltzing with the Versatile Platform of Graphene to Synthesize Composite Photocatalysts", Chem Rev, 115, 10307-10377 (2015).

[13] Low, J., Yu, J. and Ho, W., "Graphene-Based Photocatalysts for CO_2 Reduction to Solar Fuel", J Phys Chem Lett, 6, 4244-4251 (2015).

[14] Geim, A. K. and Novoselov, K. S., "The rise of graphene", Nat Mater, 6, 183-191 (2007).

[15] Morozov, S. V., Novoselov, K. S., Katsnelson, M. I., Schedin, F., Elias, D. C., Jaszczak, J. A. and Geim, A. K., "Giant intrinsic carrier mobilities in graphene and its bilayer", Phys Rev Lett, 100, 016602 (2008).

[16] Chae, H. K., Siberio-Perez, D. Y., Kim, J., Go, Y., Eddaoudi, M., Matzger, A. J., O'Keeffe, M. and Yaghi, O. M., "A route to high surface area, porosity and inclusion of large molecules in crystals", Nature, 427, 523-527 (2004).

[17] Lee, C., Wei, X. D., Kysar, J. W. and Hone, J., "Measurement of the elastic properties and intrinsic strength of monolayer graphene", Science, 321, 385-388 (2008).

[18] Balandin, A. A., Ghosh, S., Bao, W. Z., Calizo, I., Teweldebrhan, D., Miao, F. and Lau, C. N., "Superior thermal conductivity of single-layer graphene", Nano Lett, 8, 902-907 (2008).

[19] Nair, R. R., Blake, P., Grigorenko, A. N., Novoselov, K. S., Booth, T. J., Stauber, T., Peres, N. M. R. and Geim, A. K., "Fine structure constant defines visual transparency of graphene", Science, 320, 1308-1308 (2008).

[20] Lu, C.-C., Lin, Y.-C., Yeh, C.-H., Huang, J.-C. and Chiu, P.-W., "High Mobility Flexible Graphene Field-Effect Transistors with Self-Healing Gate Dielectrics", Acs Nano, 6, 4469-4474 (2012).

[21] Tsai, L.-W. and Tai, N.-H., "Enhancing the Electrical Properties of a Flexible Transparent Graphene-Based Field-Effect Transistor Using Electropolished Copper Foil for Graphene Growth", Acs Appl Mater Inter, 6, 10489-10496 (2014).

[22] Zhao, Y., Li, X.-g., Zhou, X. and Zhang, Y.-n., "Review on the graphene based optical fiber chemical and biological sensors", Sensors and Actuators B: Chemical, 231, 324-340 (2016).

[23] Kuila, T., Mishra, A. K., Khanra, P., Kim, N. H. and Lee, J. H., "Recent advances in the efficient reduction of graphene oxide and its application as energy storage electrode materials", Nanoscale, 5, 52-71 (2013).

[24] Goenka, S., Sant, V. and Sant, S., "Graphene-based nanomaterials for drug delivery and tissue engineering", J Control Release, 173, 75–88 (2014).

[25] Yu, M., Li, R., Wu, M. and Shi, G., "Graphene materials for lithium–sulfur batteries", Energy Storage Materials, 1, 51-73 (2015).

[26] Yang, J. and Gunasekaran, S., "Electrochemically reduced graphene oxide sheets for use in high performance supercapacitors", Carbon, 51, 36-44 (2013).

[27] Nekahi, A., Marashi, P. H. and Haghshenas, D., "Transparent conductive thin film of ultra large reduced graphene oxide monolayers", Appl Surf Sci, 295, 59-65 (2014).

[28] Seo, J.-T., Han, J., Lim, T., Lee, K.-H., Hwang, J., Yang, H. and Ju, S., "Fully Transparent Quantum Dot Light-Emitting Diode Integrated with Graphene Anode and Cathode", Acs Nano, 8, 12476-12482 (2014).

[29] Kim, S. B., Park, J. Y., Kim, C. S., Okuyama, K., Lee, S. E., Jang, H. D. and Kim, T. O., "Effects of Graphene in Dye-Sensitized Solar Cells Based on Nitrogen-Doped TiO_2 Composite", J Phys Chem C, 119, 16552-16559 (2015).

[30] Han, G. S., Song, Y. H., Jin, Y. U., Lee, J.-W., Park, N.-G., Kang, B. K., Lee, J.-K., Cho, I. S., Yoon, D. H. and Jung, H. S., "Reduced Graphene Oxide/Mesoporous TiO_2 Nanocomposite Based Perovskite Solar Cells", Acs Appl Mater Inter, 7, 23521-23526 (2015).

[31] Castro Neto, A. H., "The carbon new age", Mater Today, 13, 12-17 (2010).

[32] Thickett, S. C. and Zetterlund, P. B., "Functionalization of Graphene Oxide for the Production of Novel Graphene-Based Polymeric and Colloidal Materials", Curr Org Chem, 17, 956-974 (2013).

[33] Tan, L. L., Chai, S. P. and Mohamed, A. R., "Synthesis and Applications of Graphene-Based TiO_2 Photocatalysts", Chemsuschem, 5, 1868-1882 (2012).

[34] Kaniyoor, A. and Ramaprabhu, S., "A Raman spectroscopic investigation of graphite oxide derived graphene", Aip Adv, 2, 032183 (2012).

[35] Eda, G. and Chhowalla, M., "Chemically Derived Graphene Oxide: Towards Large-Area Thin-Film Electronics and Optoelectronics", Adv Mater, 22, 2392-2415 (2010).

[36] Malard, L. M., Pimenta, M. A., Dresselhaus, G. and Dresselhaus, M. S., "Raman spectroscopy in graphene", Phys Rep, 473, 51-87 (2009).

[37] Dreyer, D. R., Todd, A. D. and Bielawski, C. W., "Harnessing the chemistry of graphene oxide", Chem Soc Rev, 43, 5288-5301 (2014).

[38] Bhirud, A. P., Sathaye, S. D., Waichal, R. P., Ambekar, J. D., Park, C. J. and Kale, B. B., "In-situ preparation of N-TiO_2/graphene nanocomposite and its enhanced photocatalytic hydrogen production by H_2S splitting under solar light", Nanoscale, 7, 5023-5034 (2015).

[39] Zhang, L., Li, N., Jiu, H., Qi, G. and Huang, Y., "ZnO-reduced graphene oxide nanocomposites as efficient photocatalysts for photocatalytic reduction of CO_2", Ceram Int, 41, 6256-6262 (2015).

[40] Zhang, K., Shi, X., Kim, J. K., Lee, J. S. and Park, J. H., "Inverse opal structured α-Fe_2O_3 on graphene thin films: enhanced photo-assisted water splitting", Nanoscale, 5, 1939-1944 (2013).

[41] Benjwal, P., Kumar, M., Chamoli, P. and Kar, K. K., "Enhanced photocatalytic degradation of methylene blue and adsorption of arsenic(III) by reduced graphene oxide (rGO)-metal oxide (TiO_2/Fe_3O_4) based nanocomposites", Rsc Adv, 5, 73249-73260 (2015).

[42] Rong, X., Qiu, F., Zhang, C., Fu, L., Wang, Y. and Yang, D., "Adsorption-photodegradation synergetic removal of methylene blue from aqueous solution by NiO/graphene oxide nanocomposite", Powder Technol, 275, 322-328 (2015).

[43] Tang, L., Nguyen, V. H., Lee, Y. R., Kim, J. and Shim, J.-J., "Photocatalytic activity of reduced graphene oxide/SnO_2 nanocomposites prepared in ionic liquid", Synthetic Met, 201, 54-60 (2015).

[44] Bin, Z. and Hui, L., "Three-dimensional porous graphene-Co_3O_4 nanocomposites for high performance photocatalysts", Appl Surf Sci, 439-444 (2015).

[45] Hurtado, L., Reyna Natividad and García, H., "Photocatalytic activity of Cu_2O supported on multi layers graphene for CO_2 reduction by water under batch and continuous flow", Catal Commun, 84, 30-35 (2016).

[46] Wang, P.-Q., Bai, Y., Luo, P.-Y. and Liu, J.-Y., "Graphene-WO_3 nanobelt composite: Elevated conduction band toward photocatalytic reduction of CO_2 into hydrocarbon fuels", Catal Commun, 38, 82-85 (2013).

[47] Li, Q., Li, X., Wageh, S., Al-Ghamdi, A. A. and Yu, J., "CdS/Graphene Nanocomposite Photocatalysts", Adv Funct Mater, 5, 1500010 (2015).

[48] Sookhakian, M., Amin, Y. M. and Basirun, W. J., "Hierarchically ordered macro-mesoporous ZnS microsphere with reduced graphene oxide supporter for a highly efficient photodegradation of methylene blue", Appl Surf Sci, 283, 668-677 (2013).

[49] Zhou, M., Han, D., Liu, X., Ma, C., Wang, H., Tang, Y., Huo, P., Shi, W., Yan, Y. and Yang, J., "Enhanced visible light photocatalytic activity of alkaline earth metal ions-doped CdSe/rGO photocatalysts synthesized by hydrothermal method", Applied Catalysis B: Environmental, 172-173, 174-184 (2015).

[50] Wang, A., Shen, S., Zhao, Y. and Wu, W., "Preparation and characterizations of $BiVO_4$/reduced graphene oxide nanocomposites with higher visible light reduction activities", J Colloid Interf Sci, 445, 330-336 (2015).

[51] Xiang, Q., Yu, J. and Jaroniec, M., "Synergetic Effect of MoS_2 and Graphene as Cocatalysts for Enhanced Photocatalytic H2 Production Activity of TiO_2 Nanoparticles", J Am Chem Soc, 134, 6575-6578 (2012).

[52] Ong, W.-J., Tan, L.-L., Chai, S.-P., Yong, S.-T. and Mohamed, A. R., "Surface charge modification via protonation of graphitic carbon nitride (g-C_3N_4) for electrostatic self-assembly construction of 2D/2D reduced graphene oxide (rGO)/g-C_3N_4 nanostructures toward enhanced photocatalytic reduction of carbon dioxide to methane", Nano Energy, 13, 757-770 (2015).

[53] Zhang, Y., Tang, Z.-R., Fu, X. and Xu, Y.-J., "TiO_2-Graphene Nanocomposites for Gas-Phase Photocatalytic Degradation of Volatile Aromatic Pollutant: Is TiO_2-Graphene Truly Different from Other TiO_2-Carbon Composite Materials?", Acs Nano, 4, 7303-7314 (2010).

[54] Zhang, N., Zhang, Y., Pan, X., Yang, M.-Q. and Xu, Y.-J., "Constructing Ternary CdS-Graphene-TiO_2 Hybrids on the Flatland of Graphene Oxide with Enhanced Visible-Light Photoactivity for Selective Transformation", 116, 18023-18031 (2012).

[55] Perera, S. D., Mariano, R. G., Vu, K., Nour, N., Seitz, O., Chabal, Y. and Kenneth J. Balkus, J., "Hydrothermal Synthesis of Graphene-TiO_2 Nanotube Composites with Enhanced Photocatalytic Activity", Acs Catal, 2, 949-956 (2012).

[56] Zhang, Y., Zhang, N., Tang, Z.-R. and Xu, Y.-J., "Graphene Transforms Wide Band Gap ZnS to a Visible Light Photocatalyst. The New Role of Graphene as a Macromolecular Photosensitizer", Acs Nano, 6, 9777-9789 (2012).

[57] Yang, M. Q. and Xu, Y. J., "Basic Principles for Observing the Photosensitizer Role of Graphene in the Graphene-Semiconductor Composite Photocatalyst from a Case Study on Graphene-ZnO", J Phys Chem C, 117, 21724-21734 (2013).

[58] Yeh, T. F., Cihlar, J., Chang, C. Y., Cheng, C. and Teng, H. S., "Roles of graphene oxide in photocatalytic water splitting", Mater Today, 16, 78-84 (2013).

[59] Ng, Y. H., Lightcap, I. V., Goodwin, K., Matsumura, M. and Kamat, P. V., "To What Extent Do Graphene Scaffolds Improve the Photovoltaic and Photocatalytic Response of TiO_2 Nanostructured Films?", J Phys Chem Lett, 1, 2222-2227 (2010).

[60] Zou, W., Zhang, L., Liu, L., Wang, X., Sun, J., Wu, S., Deng, Y., Tang, C., Gao, F. and Dong, L., "Engineering the Cu_2O-reduced graphene oxide interface to enhance photocatalytic degradation of organic pollutants under visible light", Applied Catalysis B: Environmental, 181, 495-503 (2016).

[61] Babu, S. G., Vinoth, R., Neppolian, B., Dionysiou, D. D. and Ashokkumar, M., "Diffused sunlight driven highly synergistic pathway for complete mineralization of organic contaminants using reduced graphene oxide supported photocatalyst", J Hazard Mater, 291, 83-92 (2015).

[62] Almeida, B. M., Melo, M. A., Bettini, J., Benedetti, J. E. and Nogueira, A. F., "A novel nanocomposite based on TiO_2/Cu_2O/reduced graphene oxide with enhanced solar-light-driven photocatalytic activity", Appl Surf Sci, 324, 419-431 (2015).

[63] Mishra, M. and Chun, D. M., "α-Fe_2O_3 as a photocatalytic material: A review", Appl Catal a-Gen, 498, 126-141 (2015).

[64] Wang, L., Wen, M., Wang, W., Momuinou, N., Wang, Z. and Li, S., "Photocatalytic degradation of organic pollutants using rGO supported TiO_2-CdS composite under visible light irradiation", J Alloy Compd, 683, 318-328 (2016).

[65] Moniz, S. J. A., Shevlin, S. A., Martin, D. J., Guo, Z.-X. and Tang, J., "Visible-light driven heterojunction photocatalysts for water splitting – a critical review", Energ Environ Sci, 8, 731-759 (2015).

[66] Ahn, H.-J., Kwak, M.-J., Lee, J.-S., Yoon, K.-Y. and Jang, J.-H., "Nanoporous hematite structures to overcome short diffusion lengths in water splitting", J Mater Chem A, 2, 19999-20003 (2014).

[67] Inoue, T., Fujishima, A., Konishi, S. and Honda, K., "Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders", Nature, 277, 637-638 (1979).

[68] Marszewski, M., Cao, S., Yu, J. and Jaroniec, M., "Semiconductor-based photocatalytic CO_2 conversion", Materials Horizons, 2, 261-278 (2015).

[69] Roy, S. C., Varghese, O. K., Paulose, M. and Grimes, C. A., "Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons", Acs Nano, 4, 1259-1278 (2010).

[70] Zhang, Q., Lin, C.-F., Jing, Y. H. and Chang, C.-T., "Photocatalytic reduction of carbon dioxide to methanol and formic acid by graphene-TiO_2", Journal of the Air & Waste Management Association, 64, 578-585 (2014).

[71] Wang, W.-N., Jiang, Y., Fortner, J. D. and Biswas, P., "Nanostructured Graphene-Titanium Dioxide Composites Synthesized by a Single-Step Aerosol Process for Photoreduction of Carbon Dioxide", Environ Eng Sci, 31, 428-434 (2014).

[72] Hasan, M. R., Hamid, S. B. A., Basirun, W. J., Suhaimy, S. H. M. and Mat, A. N. C., "A sol-gel derived, copper-doped, titanium dioxide-reduced graphene oxide nanocomposite electrode for the photoelectrocatalytic reduction of CO_2 to methanol and formic acid", Rsc Adv, 5, 77803-77813 (2015).

[73] Kakiage, K., Aoyama, Y., Yano, T., Oya, K., Fujisawab, J.-i. and Hanaya, M., "Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes", Chem Commun, 51, 15894--15897 (2015).

[74] Lv, T., Pan, L., Liu, X. and Sun, Z., "Visible-light photocatalytic degradation of methyl orange by CdS-TiO_2-Au composites synthesized via microwave-assisted reaction", Electrochim Acta, 83, 216-220 (2012).

[75] Kalanur, S. S., Hwang, Y. J. and Joo, O.-S., "Construction of efficient CdS-TiO_2 heterojunction for enhanced photocurrent, photostability, and photoelectron lifetimes", J Colloid Interf Sci, 402, 94-99 (2013).

[76] Leary, R. and Westwood, A., "Carbonaceous nanomaterials for the enhancement of TiO2 photocatalysis", Carbon, 49, 741-772 (2011).

[77] Dai, K., Peng, T. Y., Ke, D. N. and Wei, B. Q., "Photocatalytic hydrogen generation using a nanocomposite of multi-walled carbon nanotubes and TiO_2 nanoparticles under visible light irradiation", Nanotechnology, 20, 125603 (2009).

[78] Cong, Y., Li, X. K., Dong, Z. J., Yuan, G. M., Cui, Z. W. and Zhang, J., "Core-shell structured carbon black@TiO_2 microsphere with enhanced visible light photocatalytic activity", Mater Lett, 138, 200-203 (2015).

[79] Sun, M. X., Ma, X. Q., Chen, X., Sun, Y. J., Cui, X. L. and Lin, Y. H., "A nanocomposite of carbon quantum dots and TiO_2 nanotube arrays: enhancing photoelectrochemical and photocatalytic properties", Rsc Adv, 4, 1120-1127 (2014).

[80] Ranganathan, K., Morais, A., Nongwe, I., Longo, C., Nogueira, A. F. and Coville, N. J., "Study of photoelectrochemical water splitting using composite films based on TiO_2 nanoparticles and nitrogen or boron doped hollow carbon spheres as photoanodes", J Mol Catal a-Chem, http://dx.doi.org/10.1016/j.molcata.2015.10.024, (2015).

[81] de Morais, A., Loiola, L. M. D., Benedetti, J. E., Goncalves, A. S., Avellaneda, C. A. O., Clerici, J. H., Cotta, M. A. and Nogueira, A. F., "Enhancing in the performance of dye-sensitized solar cells by the incorporation of functionalized multi-walled carbon nanotubes into TiO_2 films: The role of MWCNT addition", J Photoch Photobio A, 251, 78-84 (2013).

[82] Xiang, Q., Cheng, B. and Yu, J., "Graphene-Based Photocatalysts for Solar-Fuel Generation", Angewandte Chemie International Edition, 54, 11350 -11366 (2015).

[83] Yang, N. L., Zhai, J., Wang, D., Chen, Y. S. and Jiang, L., "Two-Dimensional Graphene Bridges Enhanced Photoinduced Charge Transport in Dye-Sensitized Solar Cells", Acs Nano, 4, 887-894 (2010).

[84] Liu, Y., Li, D. and Sun, S., "Pt-based composite nanoparticles for magnetic, catalytic, and biomedical applications", J Mater Chem, 21, 12579-12587 (2011).

[85] Benedetti, J. E., Bernardo, D. R., Morais, A., Bettini, J. and Nogueira, A. F., "Synthesis and characterization of a quaternary nanocomposite based on TiO_2/CdS/rGO/Pt and its application in the photoreduction of CO_2 to methane under visible light", Rsc Adv, 5, 33914-33922 (2015).

[86] Fujishima, A. and Honda, K., "Electrochemical Photolysis of Water at a Semiconductor Electrode", Nature, 238, 37-38 (1972).

[87] Walter, M. G., Warren, E. L., McKone, J. R., Boettcher, S. W., Mi, Q. X., Santori, E. A. and Lewis, N. S., "Solar Water Splitting Cells", Chem Rev, 110, 6446-6473 (2010).

[88] Carminati, S. A., Souza, F. L. and Nogueira, A. F., "Enhancing hematite photoanode activity for water oxidation by incorporation of reduced graphene oxide", Chemphyschem, 17, 170-177 (2016).

[89] Morais, A., Longo, C., Araujo, J. R., Barroso, M., Durrant, J. R. and Nogueira, A. F., "Nanocrystalline anatase TiO_2/reduced graphene oxide composite films as photoanodes for photoelectrochemical water splitting studies: the role of the reduced graphene oxide ", Phys Chem Chem Phys, 18, 2608-2616 (2016).

[90] Meng, F. K., Li, J. T., Cushing, S. K., Bright, J., Zhi, M. J., Rowley, J. D., Hong, Z. L., Manivannan, A., Bristow, A. D. and Wu, N. Q., "Photocatalytic Water Oxidation by Hematite/Reduced Graphene Oxide Composites", Acs Catal, 3, 746-751 (2013).

[91] Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V. and Firsov, A. A., "Electric field effect in atomically thin carbon films", Science, 306, 666-669 (2004).