Interactions between graphene oxide and wide band gap semiconductors

M Kawa[1,2], A Podborska[3], K Szaciłowski[2]

[1] Faculty of Energy and Fuels, AGH University of Science and Technology, Ave. Mickiewicza 30, 30-059 Krakow, Poland

[2] Academic Centre for Materials and Nanotechnology, AGH University of Science and Technology, Ave. Mickiewicza 30, 30-059Krakow, Poland

[3] Faculty of Non-Ferrous Metals, AGH University of Science and Technology, Ave. Mickiewicza 30, 30-059Krakow, Poland

E-mail: mkawa@agh.edu.pl

Abstract. The graphene oxide (GO) and GO@TiO_2 nanocomposite have been synthesised by using modified Hummers method and ultrasonics respectively. The materials were characterized by using X-ray diffraction, Fourier transform infrared spectroscopy and UV-Vis absorption spectroscopy. It was found that the interaction between GO and TiO_2 affects the average interlayer spacing in carbonaceous material. The formation of bonds between various oxygen-containing functional groups and surface of titanium dioxide was investigated. One of them formed between the quinone structures (occur in graphene oxide) and titanium atoms exhibited 1.5 bond order. Furthermore the charge-transfer processes in GO@TiO_2 composite were observed.

1. Introduction

Micro- and nanoelectronics continually search for new semiconducting materials of unusual properties. Scientists try to modify well known materials with different organic and inorganic compounds to get new materials with unique properties. One of the most popular example is titanium dioxide (TiO_2). Is a very well know wide band gap semiconductor. It is stable has low price and good performance. Moreover, it is chemically inert and nontoxic. All these properties caused that TiO_2 is widely used as photocatalyst [1-3], in dye-sensitized solar cells [4, 5], and in construction of memristors [6, 7] or materials for molecular logic devices [8, 9].

Other examples of very interesting materials are graphene and graphene oxide (GO). Graphene is a flat monolayer of sp^2-bonded carbon atoms. It has excellent mobility of charge carriers, high thermal conductivity, a large specific surface area and good mechanical stability. What is more the surface of graphene oxide is easily functionalized in comparison with other nanocarbon materials (carbon nanotubes or fullerenes). Graphene and graphene oxide find great application in catalysis, energy conversion, sensors or nanoelectronics. [10, 11]

It is therefore justified that scientists have tried to combine these two materials: semiconductors and graphene oxide. A variety of semiconductors have been used to synthesis of graphene/graphene oxide based composites. They mainly include metal oxides, metal sulphides or metallates (Fig. 1.) [10-12].
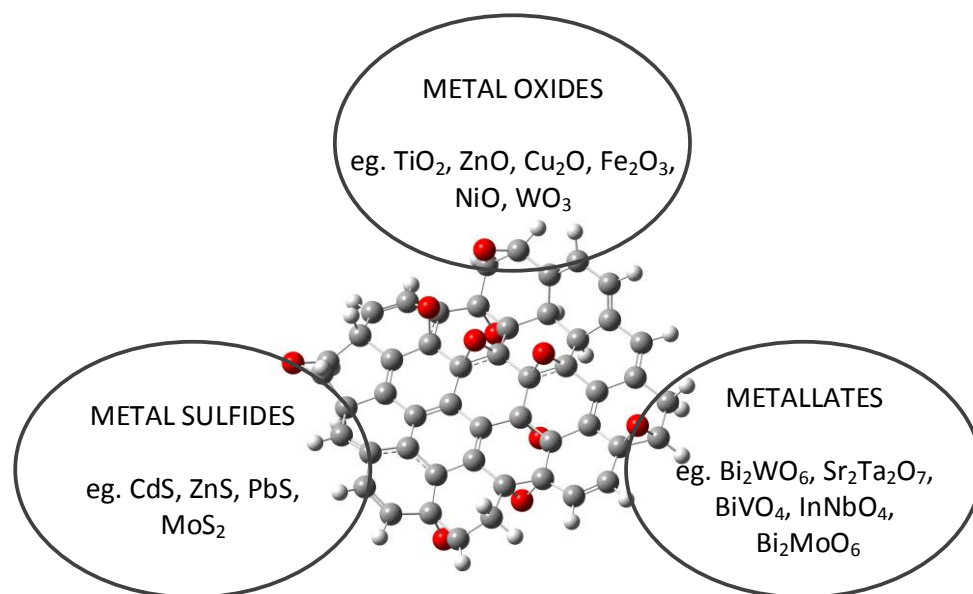
Figure 1. Composites of graphene oxide with different semiconductors.

Composites based on graphene materials and semiconductors exhibit many interesting properties. First of all, the presence of carbonaceous material contributes to the effective separation between the electron and the hole that are produced as a result of photoexcitation. Separated electron-hole pairs can lead to increase of photovoltaic efficiency but may also undergo recombination processes. Secondly, graphene oxide adsorbed at the surface of semiconductors can increase the absorption range due to formation of charge-transfer complexes. Shift of the absorption band toward lower wavenumber is very important for applications in photovoltaic or photocatalysis. Finally, composite materials increase the interaction area and adsorption of pollutants and dyes with photocatalyst by creating a π-π interaction with the delocalized electrons of graphene-based compounds. [11, 13]

1.1 Structural feature of graphene oxide

Graphene oxide is an amorphous material consisting of the corrugated carbon backbone and various oxygen-containing functional groups which are located mainly at the top and edges of flakes. Both the quantity and type of functional groups to a large extend depend on synthesis conditions. One of the most common methods used to obtain graphene oxide is Hummers method [14]. Graphene oxide is obtained by oxidation of graphite in a strong acidic medium using potassium permanganate as the oxidising agent. By applying a milder oxidant or a stepwise oxidation the adjusting of oxidation degree of graphene oxide is possible. The backbone of graphene oxide in comparison with pristine graphene is made up both sp^2 and sp^3 carbon atoms witch significantly disrupted aromaticity. Therefore graphene oxide behaves as a semiconductor. So far many of models describing structural of graphene oxide have been proposed. One of them, considering majority of oxygen-containing functional groups is the Lerf-Klinowski model [15] (Fig. 2a). This model assumes a nonstoichiometric atomic composition. Functional group such as: hydroxyl, epoxy or carboxylic acids are irregularly distributed at the top, bottom and edges of graphene oxide flakes. Furthermore NMR studies reveal that between GO and water molecules occur very strong interactions. That is probably a key factor in keeping the stacked structure of GO (Fig. 2b).
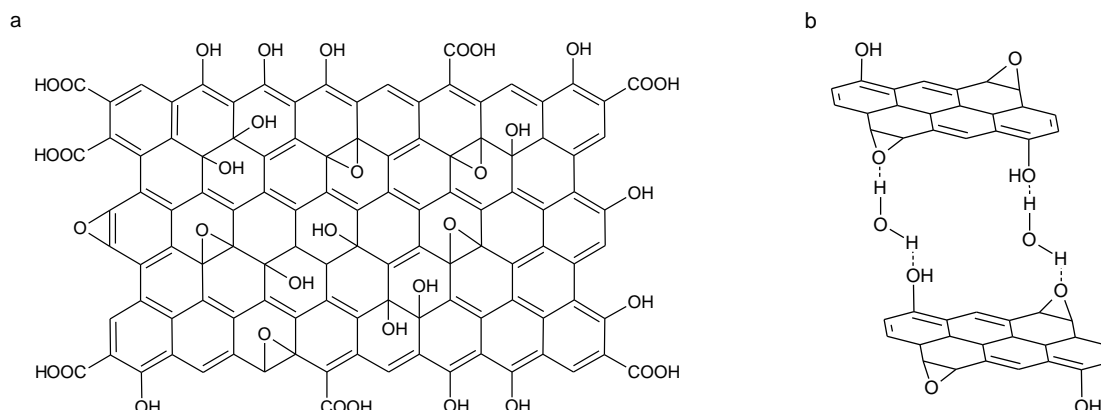
Figure 2. The Lerf-Klinowski model of graphene oxide (a), hydrogen bonding network formed between oxygen-containing functional groups and water (b).

1.2 TiO$_2$-graphene oxide system

Graphene oxide due to the large amount of the oxygen-containing functional groups can act as a chelating or bridging ligand. *P. Kwolek et al.* [15] have demonstrated the capability of interactions between catechol and TiO$_2$. Due to the presence of vicinal hydroxyl groups in GO similar considerations for GO@TiO$_2$ system can be carried out. When the graphene oxide flakes come in contact with surface of TiO$_2$ a ligand-exchange reaction occurs. Titanium atoms present on the surface of the semiconductor grains can be coordinated in two ways: two oxygen atoms originating from neighbouring functional groups coordinate the same titanium atom (the bidentate chelating structure) or two adjacent titanium sites (the bidentate bridging structure). (Fig. 3).
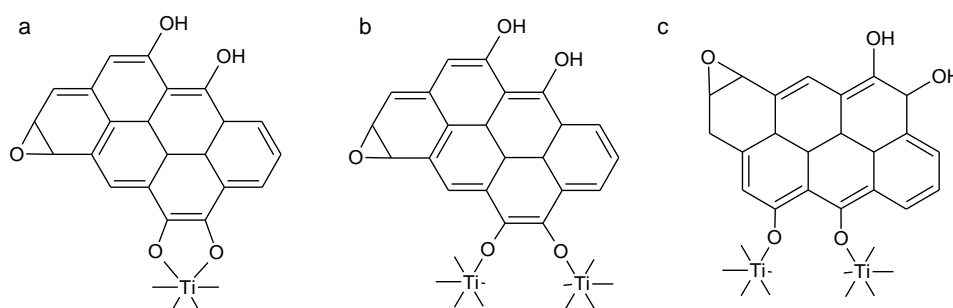

Figure 3. Surface complexes of the titanium dioxide with a graphene oxide flakes. Bidentate chelating structure (a) and bidentate bridging structure: bonds between titanium atoms and vicinal hydroxyl groups (b) or hydroxyl groups separated by a carbon atom (c).

Due to the presence of hydroxyl groups on the surface and edges of the graphene oxide flakes the efficient coating of the semiconductor grains is possible. Therefore the high yield of charge-transfer processes can be expected.

2. Experimental

2.1. Synthesis of graphene oxide

The modified Hummers method was applied to oxidize graphite powder to obtain graphene oxide. In brief, 180 mL of concentrated H$_2$SO$_4$ was added to a 500 mL flask containing 6 g of graphite and 6 g of KNO$_3$ in an ice bath. Then 18 g of KMnO$_4$ was slowly added to the suspension with continuous stirring. During addiction of the oxidant the temperature of the mixture was maintained below 275 K. After that the suspension was vigorously stirred for an additional 15 minutes. Subsequently the ice

bath was removed, the mixture was warmed up to 308 K and continuous stirring for 7 h. Then 180 mL of demineralized water was added and the suspension was maintained at 353 K for another 15 minutes. Followed the mixture was cooled and the reaction was terminated by slow addition of 24 mL of H_2O_2 (30%). In the first step of the GO purification process the excess of H_2SO_4 was removed by three-fold dilution (250 ml of demineralized water) and pouring the supernatant off. Subsequent the product was purified by centrifugation (6000 rpm for 5 min three times) using solvents: 1 mol/dm^3 HCl, demineralized water, 2-propanol, tetrahydrofuran and finally toluene. The final product was dried on a hot plate at 323 K.

2.2. Synthesis of GO@TiO$_2$ nanocomposite
GO@TiO$_2$ was obtained by following procedure: 50 mg of graphene oxide was sonicated for 15 min in 20 mL of acetonitrile. Then 1.00 g of titanium dioxide (P25) was added and the suspension and sonicated for 15 minute once again. The product was centrifuged using water for 5 min three times and dried with a vacuum dryer.

3. Materials characterization
X-ray power diffraction (XRD) patterns were obtained with Cu Kα radiation in the 2θ range from 5° to 80° with a step size of 0.5°/min. FTIR measurements were carried out by using single reflection diamond ATR accessory in the transmittance mode in the range 500−4000 cm^{-1} (Bruker instrument, TENSOR II). The UV-Vis absorption spectrum was recorded with the use of Agilent 8454 UV-Vis spectrophotometer.

4. Results and discussion
The figure 4 displays the X-ray powder diffraction (XRD) patterns of the GO obtained by modified Hummers method, TiO$_2$ and GO@TiO$_2$. The main diffraction peak observed at $2\theta = 9.33°$ in the XRD pattern of pristine GO corresponding to an average interlayer spacing of ~0.95 nm. The XRD pattern of GO@TiO$_2$ beside typical peaks of anatase and rutile phase [17] shows low intensity peak at $2\theta = 12.25°$ (~0.72 nm) characteristic of GO. The smaller interlayer spacing can suggest strong interaction between graphene oxide nanoflakes at the surface of the semiconductor.
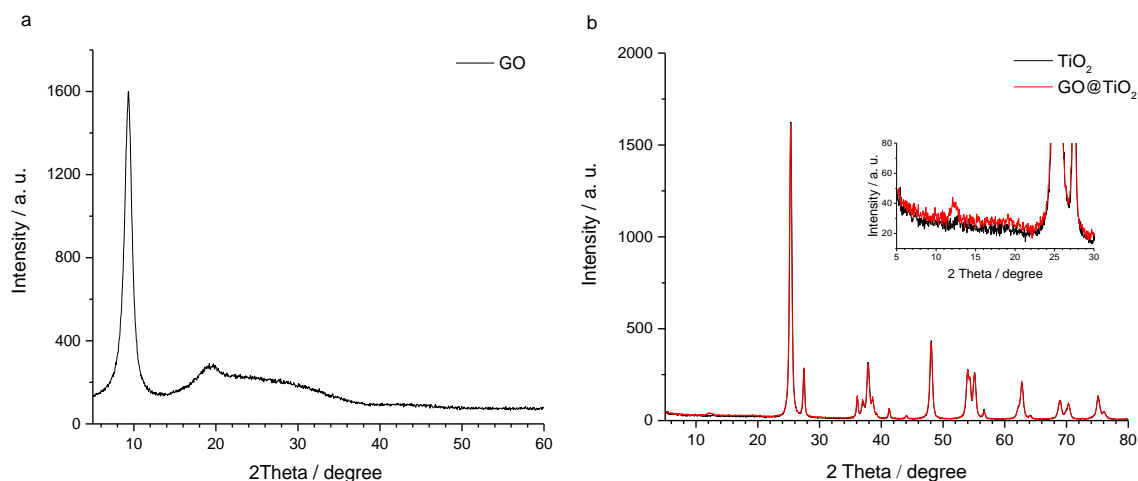

Figure 4. XRD patterns for the graphene oxide (a), pure TiO$_2$ and GO@TiO$_2$ (b).

FTIR spectrum of GO and difference spectrum (GO@P25-P25) are shown in figure 5a. The most characteristic absorption bands of GO such as the –OH broad stretching peak at 3700 – 2800 cm^{-1}, the C=O stretching vibration peat at 1724 cm^{-1}, the stretching peat of C=C at 1622 cm^{-1}, the deformation peak of O-H groups at 1356 cm^{-1}, the stretching peak of C-O-C at 1222 cm^{-1} and the C-O stretching

peak at 1048 cm^{-1} were observed. The difference spectrum reveal that the C-O stretching peak was shifted to the higher wavelength region. This change may be due to formation of C-O-Ti bonds. The formation of new bonds involving hydroxyl groups originating from GO results in a decrease the intensity of peak at 1356 cm^{-1}. Therefore the emergence of a new band at 1388 cm^{-1} suggests the formation of new bonds between the graphene oxide and the surface of the semiconductor grains. The proposed mechanism is as follows: 1) Graphene oxide flake containing a quinone structure moves towards the surface of the semiconductor grain. 2) Then the C-O-Ti bond is formed and the electron transfer from the valence band to the carbon ring occurs. 3) After charge transfer the bond order of the C-O is increased to value 1.5 (Fig. 6). The presence of the new bond explains the appearance of an additional band in the FTIR spectrum.
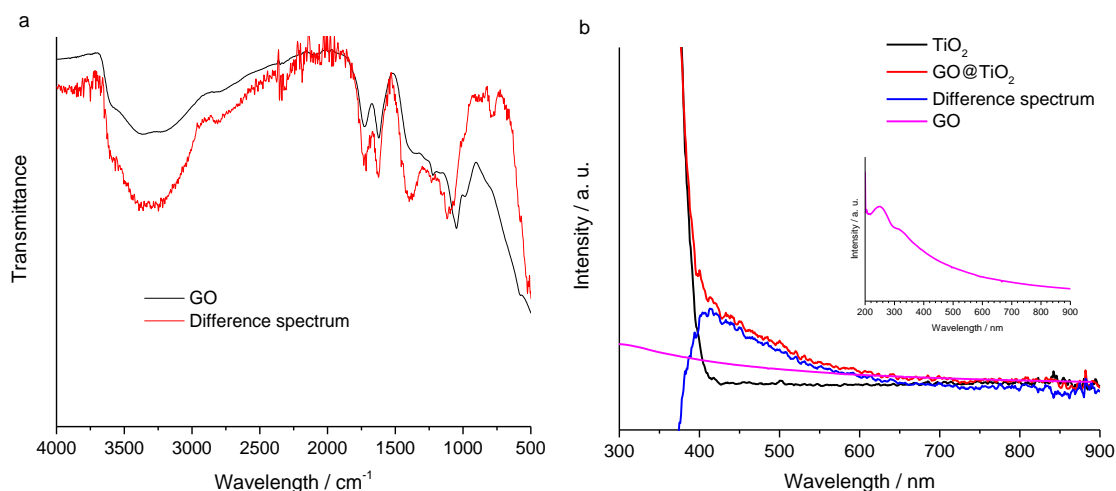

Figure 5. FTIR spectra of GO and difference spectrum (GO@TiO$_2$-TiO$_2$) (a) and UV-Vis absorption spectra of TiO$_2$, GO@TiO$_2$, GO and difference spectrum (GO@TiO$_2$-TiO$_2$) (b).
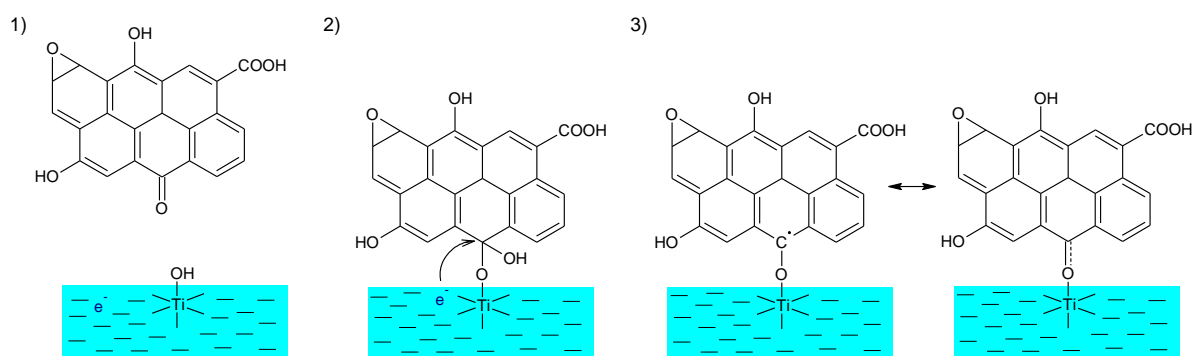

Figure 6. Mechanism of creating a new bond between the graphene oxide and the surface of TiO$_2$.

Figure 5b shows UV-Vis absorption spectra of the graphene oxide, pristine TiO$_2$, GO@TiO$_2$ composite and difference spectrum (GO@TiO$_2$-TiO$_2$). The spectrum of GO in acetonitrile solution shows two characteristic bands: at 230 nm, corresponding to the π-π* transition of aromatic C=C bonds and a shoulder at 300 nm which can be assigned to the n-π* transition of C=O bonds. Spectrum of the GO@P25 revealed increase of absorption in the visible region which is larger than would result from the total absorption of GO and TiO$_2$. Thus it can be concluded that the additional absorption is associated with the charge-transfer processes occurring between grains of semiconductor and the coordinated graphene oxide nanoflakes.

Conclusion

In this study we demonstrated the preparation of graphene oxide and GO@TiO$_2$ nanocomposite. XRD measurements confirmed the presents of GO in nanocomposite and reveal that average interlayer spacing in graphene oxide is decreased due to the interaction with the surface of TiO$_2$. The existence of bonds between titanium atoms and hydroxyl groups localized on the surface and edges of GO contributes to the efficient coating of the TiO$_2$ grains. Moreover we proved that during the formation of the GO@TiO$_2$ composite the quinone structures occur in graphene oxide flakes form new bonds with the surface of TiO$_2$ (band order is 1.5). Finally we demonstrated that the charge-transfer processes in GO@TiO$_2$ composite can occur.

Acknowledgements

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