

PHOTOCATALYTIC COMPOSITE MATERIALS BASED ON GRAPHENE AND TITANIUM OXIDE PREPARED BY DIFFERENT METHODS

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Summary: *Titanium(IV) oxide - graphene [1] or graphene oxide nano composite [2] were prepared by one-pot thermal hydrolysis of suspension graphene or graphene oxide nanosheets and titanium oxide in three different forms as a starting materials. Graphene nanosheets were produced in a large quantity from natural graphite using a high intensity cavitation field in a pressurized ultrasonic reactor [3]. The graphene oxide was prepared by improved Hummers method [4]. The direct interaction between TiO₂ nanoparticles and graphene sheet prevents the re-aggregation of the exfoliated sheets of graphene. Graphene and even graphene oxide has the ability to locally reduce the titanium to active form of Ti³⁺ ion. The graphene nanosheets make Ti³⁺ ions stable in the TiO₂ matrix and form a heterojunction system with titania.*

The better photocatalytic properties on the TiO₂-graphene oxide nanocomposite systems irrespective of light sources could be attributed to synergy effects including the increase in specific surface area with graphene oxide amount. As well as to the formation of both π - π conjugations between organic pollutants molecules and graphene skeleton and the ionic interactions between organic pollutants and oxygen-containing functional groups at the edges or on the surfaces of graphene based nanosheets. Graphene oxide works as the adsorbent, electron acceptor and photosensitizer and efficiently enhances the organic pollutants photodecomposition.

First preparation method of titanium oxide utilized thermal homogeneous hydrolysis by urea or hydrazine monohydrate. Second method used the peroxy-complex of titania as an intermediate. All these methods have own specifications and limitations. Each method provides a various morphologies and size of primary particles and aggregates with significant effects on the photocatalytic activity.

The prepared a series of samples were characterized by surface area (BET) and porosity (BJH) determination, X-ray diffraction (XRD), infrared and Raman spectroscopy (IR, RS), scanning and transmission electron microscopy (SEM, TEM) (Fig.1). UV-VIS diffuse reflectance spectroscopy was employed to estimate the band gap energies. The relative photocatalytic activity of the as-prepared thin layers of titania-graphene and titania-graphene oxide nanocomposite in poly(hydroxyethyl methacrylate) was assessed by the photocatalytic decomposition of OrangeII under UV and visible light.

1 INTRODUCTION:

Graphite is a layered hexagonal mineral. During writing by pencil a part of individual plates of graphite flakes are peeled off and remain on the paper. One atomic layer of graphite is called graphene. Graphene is a unique material permeable to light and electrons could theoretically move through a layer at a light speed.

Mechanical exfoliation, called ‘Scotch tape method’ [5] was the first method used for preparation of single-layer graphene from natural graphite. Oxidation pathway to graphene preparation starts by graphite oxidation to graphite oxide or graphene oxide using strong oxidants in the environment of strong concentrated acids. The graphite oxide was first prepared by B.C. Brodie [6] in 1859 by reaction of graphite with a mixture of potassium chlorate KClO_3 and fuming nitric acid HNO_3 . The best-known Hummers methods [7] uses a mixture of sulfuric acid, sodium nitrate NaNO_3 and potassium permanganate KMnO_4 .

Chemical exfoliation is based on graphite intercalation by various ions or molecules, such as tetrabutylammonium cations [8], 1-pyrene carboxylic acid [9] or alkalic metals in tetrahydrofuran (THF). However, the chemical modification of individual sheets disrupts the electronic properties due to significant number of defects introduced during treatments.

Liquid exfoliation uses the effect of low-intensity ultrasound and suitable solvents. The layered material is sonicated for tens hours in ultrasonic bath and individual nano-sheets are separated by centrifugation.

Another approach uses concentrated high power ultrasound instead of ultrasonic bath. Ultrasonic power is transferred to the liquid by means of sonotrode.

At atmospheric pressure can be transferred into the water marginally. To achieve higher output a liquid denser than water can be used or the pressure above the liquid can be increased. Through a liquid propagate sound waves causing alternating high-pressure and low-pressure cycles. During the low-pressure cycle, high-intensity ultrasound creates small vacuum bubbles in the liquid. When the bubbles reach a certain size, they collapse strongly during a high-pressure cycle. Implosion cause very high pressures, high temperatures and speed liquid jets are generated locally. This phenomenon is called cavitation [10]. The resulting hydrodynamic forces are able to disintegrate agglomerates and mill particles in solution.

Stationary waves are able to vibrate lamellar particles, overcome Van der Waals forces, which consequently causing that flakes are gradually peeled off to reveal individual sheets. The particle milling effect is based on intense ultrasonic cavitation, while delamination is result of stationary waves. Both, increasing the density as well as the pressure of the solvent lead to higher cavitation threshold [11, 12].

The benefits of delamination by using high-power ultrasound in a pressurized reactor, compared to delamination in an ultrasound bath, are: 1) a semi-quantitative yield of the product in a flow reactor (depending on removing the graphene phase as a foam) and a quantitative yield in a batch reactor; 2) the preparation of graphene with a low content of functional groups; and 3) possible production of tens of grams of graphene per hour.

Titanium dioxide (titania) is the most attractive photocatalyst, because it is nontoxic, chemically stable, and relatively cheap. The reported attempts to avoid the recombination of electron-hole pairs is based on the doping of titanium dioxide with noble metals, such as Pt, Au, and Pd [13, 14]. This method also proved to be less suitable because it is very difficult to determine the correct concentration of the metal. In addition, the interaction between the used metals and disassembly agent (pollutants) reduces photocatalytic efficiency. This problem can be resolved by combining titania and graphene nanosheets.

Homogeneous hydrolysis method of metal sulfates with urea is simple, low cost and very effective for preparation of nanostructured metal oxide. This method was successfully used for the preparation of photocatalytic active titania [15], In_3^+ [16], Ge^{4+} [17], Ru^{3+} [18], rare

earth [19] - doped TiO₂, boron [20] and Se and Te [21] - modified titania. In present work the samples of graphene oxide–TiO₂ nanocomposites were prepared by homogeneous hydrolysis of TiOSO₄ with urea or hydrazine monohydrate. Other method used the peroxo-complex of titania as an intermediate.

Graphene is the ideal nanostructure product to be paired with titanium dioxide, increasing its capability to absorb light as well as its photocatalytic activity [22]. In the case of graphene-TiO₂ composites, a heterojunction forms and after the photo-activation of titanium dioxide the electrons can easily transfer to the graphene nanosheets and photo-induced holes migrate into titania; recombination of e⁻ and h⁺ is strongly reduced, which increases the process yield. Pressurized bath-ultrasonic reactor (6 bar) was used to exfoliate graphite to graphene [3], which then served as precursor for synthesis of photocatalytic composite material graphene-anatase [1]. Conventional ultrasound baths cannot produce sufficiently intensive cavitation to provide graphite delamination without chemical agents, which is probably the reason why such a simple route has not yet been employed.

2 MATERIALS AND METHODS:

All chemical reagents used in the present experiments were obtained from commercial sources and used without further purification. Titanium oxo-sulfate TiOSO₄, hydrogen peroxide H₂O₂, ethylene glycol OHCH₂CH₂OH and ammonium hydroxide NH₄OH were supplied by Sigma-Aldrich. Graphene was produced in large quantity from natural graphite (Koh-i-noor Grafite Ltd. Czech republic) using high intensity cavitation field in a pressure batch-ultrasonic reactor (UIP 2000hd, 20 kHz, 2000 W, Holster Ultrasonics GmbH) [3].

The graphene prepared with ultrasound was used for synthesis of graphene oxide (GO) by improved Hummers method. Graphene oxide was prepared by our safety method, a 60 mL of H₂SO₄ and 10 mL of H₃PO₄, 1 g of graphene and 3 g of KMnO₄ were mixed in round bottom flask. The reaction was then heated to 40°C and stirred for 12 hours and pink squash suspension was obtained. Subsequently was poured onto ice with 100 ml of 30% H₂O₂. The pink squash suspension quickly changed to lemon-like yellow suspension. Reduced graphene oxide (rGO) was prepared by refluxing GO with hydrazine hydrate. GO is a non-stoichiometric material, which retains the lamellar structure of graphite. After treatment of graphene in the presence of strong acids and oxidation agents, many oxygen-containing groups such as carboxyl (C–OOH), hydroxyl (C–OH), epoxide (C–O–C) become covalently attached to its layers surfaces [23].

It was used several way of preparation TiO₂-GO nanocomposite. First was used method with urea (TiO₂U-GO), second used method with hydrazine monohydrate (TiO₂Hh-GO) and last one with hydrogen peroxo solution by titania peroxo-complex (TiO₂Per-GO).

In the typical procedure of (TiO₂Per-GO) nanocomposite preparation, 100 mL of 1.6 M titanium oxo-sulfate (TiOSO₄) was hydrolyzed by slow addition of ammonium hydroxide solution (10%) under constant stirring at temperature of 0°C in ice bath. The stirring last until the reaction mixture reaches pH 8.0. The obtained white precipitate was separated by filtration. The consequent depuration of sulfate ions from precipitate with distilled water was confirmed by the BaCl₂. The wet precipitate is mixed with 100 mL of 15% hydrogen peroxide solution; thereby a yellow solution of titania peroxo-complex is obtained. This intermediate is diluted to 1000 ml in distilled water and added a defined amount of grapheme oxide. Boiled at reflux for about 48 hours.

In the typical composite (TiO₂U-GO) preparation, 100 g of titanium sulfate TiOSO₄ was diluted in 1000 mL water acidified by 10 mL of 96% sulfuric acid. Defined quantity of GO was dispersed in reaction solution and finally 300 g of urea was added. Reaction mixture was diluted to a total volume of 4 L and under stirring was heated to 95–98°C for 6 h. The prepared samples were decanted by distilled water, filtered off and dried at 105°C.

Preparation by homogeneous hydrolysis by hydrazine monohydrate is almost similar with previous method.

Furthermore, the oxygen-containing groups also enable GO to exhibit excellent hydrophilic properties. During reaction of $\text{Ti}(\text{SO}_4)_2$ with GO, plenty of oxygen-containing groups, such as $\text{C}=\text{O}$ located in the interlayer of graphene oxide were consumed during the nucleation and growth of TiO_2 crystallites, which means graphene oxide has been partly reduced [24]. The oxygen-containing groups on the graphene oxide can interact with titanium hydroxide complex and the TiO_2 nanoparticles, resulting in hydrogen bonds between them [25].

Diffraction patterns were collected with diffractometer PANalytical X'Pert PRO equipped with conventional X-ray tube (Cu $\text{K}\alpha$ radiation, 40 kV, 30 mA) and a linear position sensitive detector PIXcel with an anti-scatter shield. A programmable divergence slit set to a fixed value of 0.5 deg, Soller slits of 0.02 rad and mask of 15 mm were used in the primary beam. A programmable anti-scatter slit set to fixed value of 0.5 deg., Soller slit of 0.02 rad and Ni beta-filter were used in the diffracted beam. Qualitative analysis was performed with the DiffracPlus Eva software package (Bruker AXS, Germany) using the JCPDS PDF-2 database [26]. For quantitative analysis of XRD patterns we used Diffrac-Plus Topas (Bruker AXS, Germany, version 4.1) with structural models based on ICSD database [27]. This program permits to estimate the weight fractions of crystalline phases and mean coherence length by means of Rietveld refinement procedure.

The morphology of sample powders was inspected by transmission electron microscopy (TEM) and the crystal structure was analyzed by electron diffraction (ED) using a 200 kV TEM microscope JEOL 2010 F. As specimen support for TEM investigations a microscopic copper grid covered by a thin transparent carbon film was used. The samples were studied in both bright field and by electron diffraction with a selecting aperture (SAED) mode at an acceleration voltage of 200 kV.

The surface areas of samples were determined from nitrogen adsorption–desorption isotherms at liquid nitrogen temperature using a Coulter SA3100 instrument with outgas 15 min at 150°C. The Brunauer–Emmett–Teller (BET) method was used for surface area calculation [28], the pore size distribution (pore diameter, pore volume and micropore surface area of the samples) was determined by the Barrett–Joyner–Halenda (BJH) method [29].

The Raman spectra were acquired with DXR Raman microscope (Thermo Scientific) with 532 nm (6 mW) laser, 32 two-second scans were accumulated with laser 532 nm (6 mW) under 10× objective of Olympus microscope.

Infrared spectra were recorded by using Thermo-Nicolet Nexus 670 FT-IR spectrometer approximately in 4000–500 and 500–50 cm^{-1} , respectively, with single-reflection horizontal accessory on Si crystal. The samples were mixed with KBr and pressed to conventional pellets at ambient conditions and measured in the transmission mode.

Diffuse reflectance UV/VIS spectra for evaluation of photo-physical properties were recorded in the diffuse reflectance mode (R) and transformed to absorption spectra through the Kubelka-Munk function [30]. A Perkin Elmer Lambda 35 spectrometer equipped with a Labsphere RSAPE- 20 integration sphere with BaSO_4 as a standard was used. The reflectance data were obtained as relative percentage reflectance to a non absorbing material (BaSO_4) which can optically diffuse light.

Photocatalytic activity of samples was assessed from the photobleaching kinetics of Orange II dye (sodium salt 4-[(2-hydroxy-1-naphtenyl)azo]-benzene sulfonic acid) in 1000 mL of aqueous slurries using a self-constructed photo-reactor [31]. It consists of a stainless steel cover and a quartz tube with a fluorescent lamp by Narva with power 13 W and a light intensity $\sim 3.5 \text{ mWcm}^{-2}$ (commercial name “Black Light”, 365 nm) and a Narva lamp with commercial name “Warm White” (emission spectrum $>400 \text{ nm}$). The emission spectra of both

light sources were shown in [20]. 0.5 g photocatalyst was dispersed in an ultrasonic bath (300 W, 35 kHz) for 10 min before use. The pH of the resulting suspension was taken as the initial value for neutral conditions and under the experiment, it was kept at a value of 7.0. Orange II dye or Reactive Black 5 dye solution was circulated by means of a membrane pump through a flow cell. The concentration of Orange II dye in the suspension was determined by measuring absorbance at 480 nm by Vis spectrophotometer ColorQuestXE. The suspension contained 5 mM of the dye at the beginning of the kinetic test, which is a substantial excess of what can be adsorbed by the catalyst. None of the two used light sources can degrade dyes without a photocatalyst. The kinetic experiment started by switching on the light source after the spectral signal of the dyes in the suspension reached a steady state; this actual initial signal was taken as a measure of the initial concentration of the dye. The sorption of the dye on the catalysts is hence irrelevant for the evaluation of the kinetic experiments.

3 RESULTS:

Using high intensity ultrasound (2000 W) and a pressurized ultrasonic reactor (6 bar) has been proven to be suitable non-oxidative method for preparation of graphene from raw graphite - directly, without acids, and importantly without the detour via GO. This method provided graphene with a yield in the order of tens of grams, which can be easily converted quantitatively to GO using a safe procedure. Scaling is not an issue, because graphene oxidation takes place at much milder and safer conditions than oxidation of graphite, making this method also less demanding to environment.

The graphene nanosheet has a dual task in the nanocomposite. First, it makes Ti^{3+} ions stable in the TiO_2 matrix, and second, it forms a heterojunction system with titania. Graphene works as a sensitizer, and TiO_2 works as a substrate in the heterojunction system. Under UV and visible light irradiation, photo-induced electrons on the titania surface can easily transfer to graphene nanosheets and, analogously, photo-induced holes on the graphene nanosheets surface would migrate into titania. In this way, the photo-induced electron-hole pairs in the catalyst, are effectively separated and the probability of electron-hole recombination is reduced. The Ti^{3+} state in the TiO_2 lattice originates from nonstoichiometry, oxygen deficiency, and ion intercalation, as well as surface adsorbed species and other surface or interface states. Ti^{3+} surface states of TiO_2 act as a photocatalytic active site and the increase of the photocatalytic activity of TiO_2 is due to the increase of Ti^{3+} concentration, occurring as a result of the titania ion valence change from Ti^{4+} to Ti^{3+} .

In the case of titania-graphene nanocomposites, a heterojunction forms at the interface, where there is a space charge separation region. Electrons have a tendency to flow from the higher to lower Fermi level. Graphene can accept the photo-excited electrons from TiO_2 . In this way, the photo-induced electron-hole pairs are effectively separated and the probability of electron-hole recombination is reduced.

The SEM images in Figure 1 show a huge difference between shapes of agglomerates in each sample. Primary particles of titanium oxide prepared by urea agglomerated into the sphere (Fig 1a). Primary particles of titanium oxide prepared from peroxo-complex created the small rice (Fig 1c). Primary particles of titanium oxide prepared by hydrazine monohydrate don't make any regular agglomerate (Fig 1b).

The measured results show that the photocatalytic decomposition of Orange II dye in the UV. The sample of titania peroxo-complex doped with 5 mL of graphene oxide (TiPer GO 5ml) has photocatalytic activity ($k_{365}=0.02933 \text{ min}^{-1}$). Which is a big shift compared with net titania peroxo-complex (TiPer) with photocatalytic activity ($k_{365}=0.01142 \text{ min}^{-1}$). In contrast, sample of titania prepared by Urea and doped with 5 mL (TiU GO 5ml) has the photocatalytic activity much higher ($k_{365}=0.06265 \text{ min}^{-1}$). The shift in compared with net sample of titania (TiU) was also much stronger ($k_{365}=0.01016 \text{ min}^{-1}$). All these data are

shown in Table 1 and kinetics of degradation Orange II dye is shown in Figure 2.

Sample	k^{365}
TiHH	0.0078
TiHH GO 3ml	0.0078
TiPer	0.0114
TiPer GO 5ml	0.0293
TiU	0.0102
TiU GO 5ml	0.0627

Table1.: Rate constants of prepared samples. Measured by degradation of OrangeII dye and UV light.

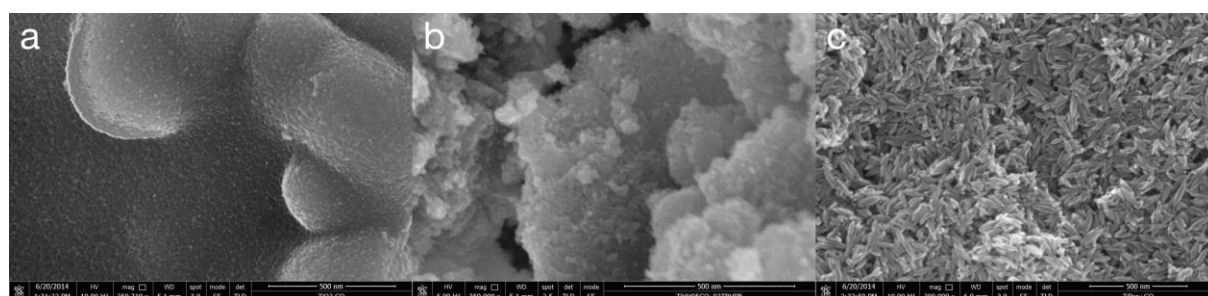


Figure 1.: SEM images of three types of titania - graphene oxide composite. Titania prepared a) by homogeneous hydrolysis by urea, b) by homogeneous hydrolysis by hydrazine monohydrate and c) with peroxo-complex intermediate.

The new method of preparation for titanium oxide by hydrazine hydrate showed some surprising findings. Although the primary particles are much smaller, doesn't form a regular agglomerates and surface area is larger the photocatalytic activity is not so better than should be expected, not in this measuring arrangement. It appears that the preparation procedure of these samples is more sensitive to conditions. We prepared the samples, which were much higher photocatalytic activity than TiU samples. But procedures has so far failed to reproducibly repeated. Also not clear yet why doping of sample does not improve photocatalytic properties significantly than that of other methods.

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ANNEXES:

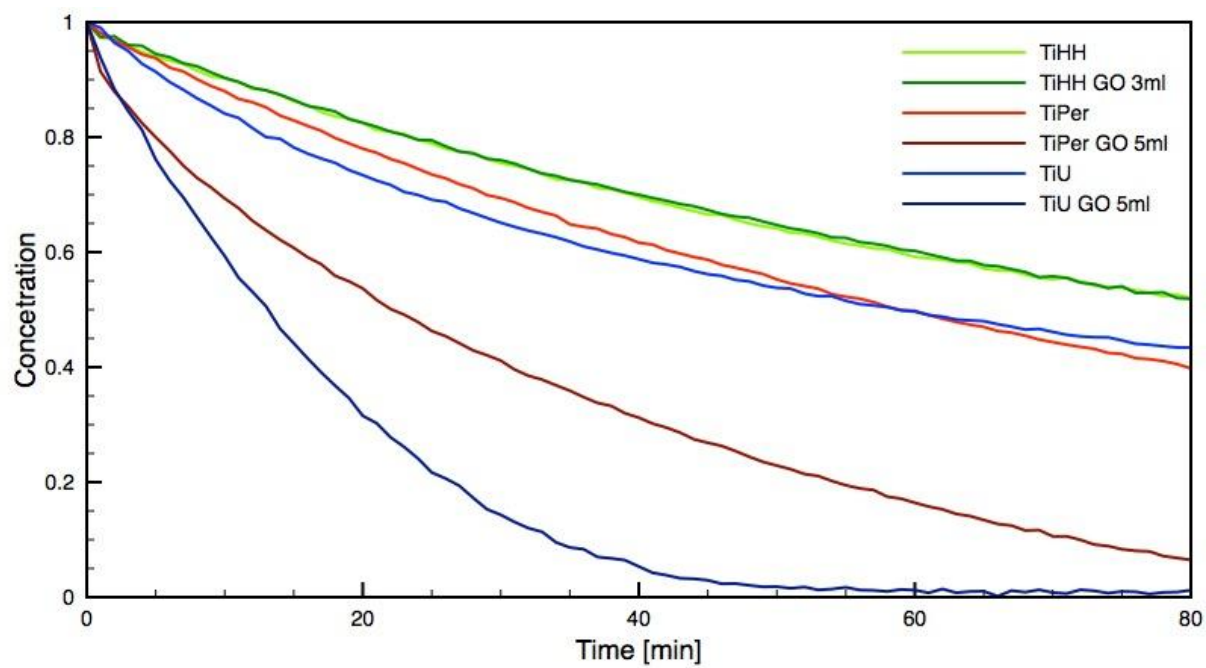


Figure 2.: Graph of kinetics of degradation Orange II dye.