



# One-pot, solvothermal synthesis of TiO<sub>2</sub>–graphene composite nanosheets

Zhe Zhang<sup>a</sup>, Wenshu Yang<sup>a</sup>, Xiaoxin Zou<sup>b</sup>, Fugang Xu<sup>a</sup>, Xiaodan Wang<sup>a</sup>, Bailin Zhang<sup>a</sup>, Jilin Tang<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

<sup>b</sup> Department of Chemistry & State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, PR China

## ARTICLE INFO

### Article history:

Received 11 June 2012

Accepted 23 July 2012

Available online 7 August 2012

### Keywords:

Graphene

TiO<sub>2</sub>

Composites

Photocatalyst

Solvothermal reaction

## ABSTRACT

In this article, we propose a facile one-pot solvothermal route for synthesizing TiO<sub>2</sub>–graphene composite nanosheets (TGCN). In the system, ethylene glycol not only as a reducing agent can convert graphene oxide to reduced graphene oxide nanosheets, but also is employed to control the hydrolysis and condensation rates of tetrabutoxytitanium. The obtained TGCN hybrid materials are characterized by atomic force microscopy, transmission electron microscopy, UV–vis spectroscopy, Raman spectroscopy, X-ray photo-electron spectroscopy, X-ray diffraction, and thermal gravimetric analysis. It is found that the quantity of H<sub>2</sub>O used in the reaction is the key to obtain high-quality product. The photocatalytic activities of the products are evaluated using the photocatalytic degradation of methylene blue (MB) as a probe reaction. The results showed that the obtained TGCN have an enhanced adsorption capacity and remarkable improvements in the photodegradation rate of MB under visible light compared to P25.

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## 1. Introduction

Graphene, a single layer of sp<sup>2</sup>-bonded carbon atoms packed into a benzene-ring structure, has recently become one of the most appealing stars in material science [1,2]. Due to its huge surface area (calculated value, 2630 m<sup>2</sup>/g), excellent electric conductivity [3,4], and mechanical strength [5,6], graphene has shown great application potential in many fields, such as electronic devices [7–9], energy storage and conversion [10–12], and biosensors [13,14]. Since the first report on graphene obtained by mechanical cleavage method in 2004 [15], a wide range of techniques for the synthesis of graphene have been reported. Among various methods, chemical or thermal conversion from graphene oxide (GO), which can be prepared from natural graphite by the modified Hummers' method [16,17], is the most suitable method for low-cost and large-scale production of graphene. In addition, the oxygen is bound to the carbon in the form of hydroxyl, epoxy, and some carbonyl functional groups in GO nanosheets [18–20], which allows for easy dispersion of GO in water and various organic solvents for further proposed applications [21].

On the other hand, as a well-known and the most investigated functional material in semiconductor photocatalysis, TiO<sub>2</sub> has been widely used in degradation of environmental pollutants [22–25]. However, there are still many challenges remaining that are yet to be met before these photocatalytic processes become economically feasible, such as suppression of the recombination of photo-generated electron–hole pairs. Considering the special charge

transfer properties of one-dimensional (1D) nanomaterials, carbon nanotubes (CNTs) were introduced into the photocatalysis as charge carriers to suppress the recombination [26–28]. However, the efficiency was increased limitedly because of the point contact between TiO<sub>2</sub> and columniform 1D CNTs [29]. On the contrary, based on the huge surface area of the graphene and good contact with TiO<sub>2</sub> nanoparticles (NPs), considerable efforts have been made to incorporate graphene into TiO<sub>2</sub>-based composite materials [30–37]. For example, Li's group obtained a chemically bonded TiO<sub>2</sub> (P25)–graphene nanocomposite photocatalyst with graphene oxide and P25, using a facile one-step hydrothermal method [30]. Dai's group prepared a graphene/TiO<sub>2</sub> nanocrystals hybrid materials by a two-step method in which TiO<sub>2</sub> was first coated on GO nanosheets by hydrolysis and crystallized into anatase nanocrystals by hydrothermal treatment in the second step [33]. However, the resulting composites are mostly in the form of aggregation due to  $\pi$ – $\pi$  stacking interactions between graphene nanosheets, in which the obtained composite materials have relatively low surface area. Furthermore, most of TiO<sub>2</sub>-based composite materials are prepared by multistep procedures, which increased the complexity of the process.

In this article, we report a simple one-pot solvothermal route for synthesizing TiO<sub>2</sub>–graphene composite nanosheets (TGCNs), which have several important benefits. (1) TiO<sub>2</sub> NPs on graphene have small size (~4 nm) and good size distribution; (2) TiO<sub>2</sub> NPs can form a uniform distribution on the surface of graphene nanosheets; (3) In the synthesis, ethylene glycol (EG) plays a dual role in obtaining TGCN. That is, EG can not only used to control the hydrolysis and condensation rates of tetrabutoxytitanium (TBOT), but also used as a reducing agent for the effective reduction of GO.

\* Corresponding author. Fax: +86 431 85262734.

E-mail address: jltang@ciac.jl.cn (J. Tang).

## 2. Experimental section

### 2.1. Chemicals

Graphite was purchased from Alfa Aesar. Poly(N-vinyl-2-pyrrolidone) (PVP K30, molecular weight = 30000–40000) and TOBT were obtained from Shanghai Chemical Factory (Shanghai, China). EG was purchased from Beijing Chemical Reagent Factory (Beijing, China). Other reagents were of analytical grade and were used as received without further purification. All aqueous solutions were prepared with Milli-Q water from a Milli-Q Plus system (Millipore).

### 2.2. Apparatus

Atomic force microscopic (AFM) images were recorded by using a SPI3800N microscope (Seiko Instruments, Inc., Japan) operating in the tapping mode with standard silicon tips (NANOSENSORS, Switzerland) at room temperature under ambient conditions. The samples were drop-cast on freshly cleaved mica and dried at room temperature. UV–vis detection was carried out on a Cary 500 UV–vis–NIR spectrophotometer (Varian, USA). Raman spectra were acquired on a Renishaw (Renishaw, United Kingdom) 2000 model confocal microscopy Raman spectrometer with 514.5 nm wavelength incident laser light. X-ray photoelectron spectroscopy (XPS) measurement was taken on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with Al K $\alpha$  X-ray radiation as the X-ray source for excitation. The sample for XPS characterization was deposited onto a Si slide. X-ray diffraction (XRD) spectra was obtained on a D8 ADVANCE (Bruker, Germany) using Cu K $\alpha$  (1.5406 Å) radiation. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained with a TECNAI G<sub>2</sub> high-resolution transmission electron microscope (FEI, Holland) with an accelerating voltage of 200 kV and Hitachi H600 electron microscope (Hitachi, Japan) with an accelerating voltage of 100 kV. The sample for TEM characterization was prepared by placing a drop of prepared solution on carbon-coated copper grid and drying at room temperature. Thermogravimetric analysis (TGA) of sample was performed on a Pyris Diamond TG/DTA thermogravimetric analyzer (Perkin-Elmer, USA). Sample was heated under an air atmosphere from room temperature to 900 °C at 10 °C/min.

### 2.3. Preparation of GO

The graphite oxide was synthesized from graphite according to the literature [38]. Then, exfoliation of graphite oxide into graphene oxide was achieved by sonication of the dispersion for 60 min (80 W, 90% amplitude). The obtained brown dispersion was then subjected to centrifugation at 3000 r.p.m for 30 min with a rotor radius of 8 cm in order to remove any unexfoliated graphite oxide. Finally, a homogeneous aqueous GO dispersion (about 0.5 mg/mL) was obtained.

### 2.4. Preparation of TGCN

In a typical synthesis, 0.1 g PVP was dissolved in 10 mL EG with stirring. Then a solution of TBOT (0.2 g) in 0.8 g of EG was injected in, and the mixture was kept stirring at room temperature for 1 h. After 3 mL of GO, aqueous dispersion (about 0.5 mg/mL) was slowly added into the above suspension and then stirred for 10 min. The mixture was transferred to a Teflon-lined stainless steel autoclave for solvothermal reaction at 150 °C for 2 h. After the solvothermal treatment was completed, the autoclave was cooled and the final product was collected by centrifugation and washed with ethanol.

### 2.5. Photocatalytic experiments

The photocatalytic activity was investigated in aqueous solution in a water-cooled quartz cylindrical cell with a 1 cm optical path length. The reaction mixture in the cell was maintained at 20 °C by a continuous flow of water and magnetic stirring, and was illuminated with an internal light source. The UV source was a 400 W high-pressure mercury lamp (main output 313 nm). The visible light source was a 500 W xenon lamp. The TGCN (20 mg) were mixed with an aqueous solution of methylene blue (MB) (200 mL,  $2.0 \times 10^{-5}$  M). The aqueous system was magnetically stirred in the dark for 1 h to allow adsorption equilibrium between the MB and TGCN to be formed and then subjected to UV or visible light irradiation. At given irradiation time intervals, a series of aqueous solutions (3 mL) were collected and centrifuged to remove the suspended catalyst particles for analysis. The concentration of the MB was analyzed on a UV/Vis spectrophotometer using its characteristic absorption at 660 nm. For comparison, the photocatalytic activity of commercial photocatalyst P25 was also measured under the same conditions.

## 3. Results and discussion

The whole preparation strategy for constructing the TGCN is shown in Scheme 1.

Firstly, TBOT was mixed with EG to form titanium glycolates or mixed alkoxide/glycolate derivatives [39]. Secondly, GO aqueous dispersion was added to the above mixture for producing TGCN via a solvothermal route. Fig. 1A shows the typical AFM image of GO. It is observed that the mica substrate is covered with a number of nanosheets with different size. The corresponding cross-sectional view (Fig. 1C) of the typical AFM image of GO (Fig. 1A) indicates that the average thickness of nanosheets is about 1 nm. The AFM image (Fig. 1B) and the corresponding cross-sectional view (Fig. 1D) of TGCN show that the as-obtained TGCN have a rougher surface and thicker average thickness than the pristine GO, which indicate that TiO<sub>2</sub> NPs are successfully loaded on the surface of graphene nanosheets. The morphology and structure of TGCN were further examined by TEM and HRTEM. Fig. 2A and B shows the typical TEM images of the product at different magnifications. The TEM images show that many small TiO<sub>2</sub> NPs with good size distribution are uniformly distributed on the graphene. The HRTEM image (Fig. 2C) indicates that these TiO<sub>2</sub> NPs are single crystal with a size of about 4 nm. The corresponding energy-dispersive X-ray (EDX) spectroscopy (Fig. 2D) of TGCN shows the peaks corresponding to C, O, and Ti elements, confirming the existence of TiO<sub>2</sub> NPs on the surface of graphene nanosheets.

Fig. 3 shows the UV–vis absorption spectra of aqueous dispersion of GO, TGCN, and P25. As shown in Fig. 3 (trace a), the GO dispersion displays a maximum absorption peak centered at 230 nm (attributed to  $\pi$ – $\pi^*$  transitions of aromatic C=C bonds) and a shoulder peak at about 300 nm (attributed to  $n$ – $\pi^*$  transitions of C=O bonds). After decoration with TiO<sub>2</sub> NPs onto the surface of graphene nanosheets and reduction by EG [40], the shoulder peak at about 300 nm disappears. In addition, there is an obvious blue shift of about 80 nm in the absorption edge of TGCN (trace b) compared to P25 (trace c). The blue shift is attributed to a quantum effect caused by the small size of TiO<sub>2</sub> NPs in the TGCN, which can also be proved from the HRTEM image of TiO<sub>2</sub> NPs (Fig. 2C) [41,42]. Raman spectroscopy is a useful non-destructive tool to distinguish ordered and disordered carbon structures. The Raman spectrum of graphene is characterized by two main features: G band is usually assigned to the E<sub>2g</sub> phonon of C sp<sup>2</sup> atoms, while D band is a breathing mode of  $\kappa$ -point photons of A<sub>1g</sub> symmetry. As shown in Fig. 4a, the Raman spectrum of

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