Simple fabrication of RGO/ TiO₂ nanocomposite with homogenous dispersion

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Abstract. Homogeneous dispersed RGO/TiO₂ nanocomposite was synthesized using precursors of graphene oxide (GO) and Ti(SO₄)₂ and reducing agent of urea solvent by situ hydrothermal reduction method. The X-ray diffractometer (XRD) and fourier transform-infrared (FTIR) spectra were used to characterize the microstructure of RGO/TiO₂ nanocomposite, and transmission electron microscope (TEM) and fieldemission scanning electron microscope (FESEM) were used observe the microtopography of RGO/TiO₂ nanocomposite. The effect of urea mass ratio on number of TiO₂ in RGO/TiO₂ nanocomposite was investigated. It is revealed that the TiO₂ nanoparticles efficiently disperse on the surface of RGO (reduced graphene oxide) sheets and RGO/TiO₂ has close interfacial contact.

1. Introduction
Graphene, a single layer of sp²-bonded carbon atoms, is a two-dimensional honeycomb lattice[1, 2]. It has recently attracted extensive interests own to its outstanding properties. For example, graphene have large specific surface area, high electrical conductivity, thermal conductivity and exceptional transparency[3, 4], which can be applied to various fields. For example, graphene can be used in nanoelectronic due to high electrical conductivity[5], and in drug delivery due to large specific surface area[6], and in photocatalysis due to outstanding adsorption activity[7] and in dye-sensitized cells due to exceptional transparency[8]. Recently, graphene can be prepared by various method, such as chemical vapor deposition (CVD)[9], epitaxial growth[10] and chemical reduction of GO[11]. Owe to the cheap raw materials of graphene oxide and simple fabrication of chemical reduction, the chemical reduction of graphene oxide has been widely used.

Graphene-based nanocomposite materials have fascinating properties and various applications. The homogenous dispersion of nanoparticles in graphene can affects the unique properties of nanocomposite materials. A lot of researchers had studied this problems and try their best to overcome this phenomenon. Luna et al. reported that TiO₂-rGO nanocomposites, as degradation agent retarded the biorecalcitrant contaminants on effluents, were synthetize via commercial TiO₂ and GO as precursors used in sustainable process, and TiO₂ homogeneously distributed on RGO surface in TiO₂-rGO nanocomposites[12]. Mojtaba et al. prepared rGO-TiO₂ nanocomposites via a simple hydrothermal method using TiO₂ powder and GO nanosheets as starting materials[13]. In addition, the well-dispersed TiO₂@reduced graphene oxide (rGO) nanocomposites was synthesized by Sohail[14], and the reporte point that the composites has better photocatalytic activities than pure TiO₂ in degradation of methylene blue.

In this work, homogeneous dispersed RGO/TiO₂ nanocomposite with Ti(SO₄)₂ and GO as starting
materials and urea solvent as a reducing agent was prepared via situ hydrothermal reduction method. The microstructures and morphology of the obtained samples were characterized by a series of test methods.

2. Experimental

2.1. Materials
Graphite was purchased from XFNANO Materials Tech (Nanjing) Co, Ltd. Titanous sulfate (Ti(SO4)2) and other reagents including H2SO4, KMnO4, K2S2O8, P2O5, H2O2, urea were supplied by Shanghai chemical Reagent Ltd. The deionized water was provided by Milli-Q (America) water purification system.

2.2. Preparation of RGO/TiO2
Homogeneous dispersed RGO/TiO2 nanocomposite was synthesized using precursors of graphene oxide (GO) and Ti(SO4)2 and reducing agent of urea solvent by situ hydrothermal reduction method. Modified Hummers method was used to synthesize Graphene oxide (GO)[15]. The 0.05 g of GO added in the 100 mL of aqueous solution and mixed solution bathed by ultrasound for 2 h to obtain homogenous dispersed GO aqueous solution (5 mg/L). RGO/TiO2 nanocomposite were prepared using 0.1 mol/l Ti(SO4)2, 5 mg/l GO aqueous solution and 0.1 mol/l urea. The preparation process of RGO/TiO2 nanocomposite is as follows, 10 ml Ti(SO4)2 solution added into 10 ml GO aqueous solution, and then the 1ml, 2ml, 4ml urea added in the mixed solutions. Subsequently, the above mixed solution was transferred to Teflon-sealed autoclave (50 ml) and then the Teflon-sealed autoclave having mix solution keep in a furnace under 80 ºC for 10 h. Then, the final products was obtained by isolating centrifugation with 6000 rpm for 10 min and washing by deionized water and ethanol and drying by furnace under 60 ºC for 2 h. The RGO/TiO2 nanocomposites was named by adding various reducing agent. When added urea solutions are 1 ml, 2 ml and 4 ml, the names of RGO/TiO2 nanocomposites are RGO/TiO2-1, RGO/TiO2-2 and RGO/TiO2-3, respectively.

2.3. Characterization
The phase structure of RGO/TiO2 nanocomposites was investigated by X-ray diffraction (XRD) patterns from X-ray diffractometer of RiGaKu using Cu Ka (λ=1.5406 Å) radiation. The atomic bond was analyzed by Fourier transform-infrared (FTIR) spectra in KBr pellets from Bruker FTIR of NiColet. The morphology of RGO/TiO2 nanocomposites was observed by fieldemission scanning electron microscope (FESEM) of FEI at a voltage of 20 kV. The micro- morphology of RGO/TiO2 nanocomposites was analyzed by transmission electron microscope (TEM) using JEM-2100F electron microscope of JEOL at a voltage of 200 KV.

3. Results and Discussion
The XRD patterns of GO, RGO/TiO2-1, RGO/TiO2-2 and RGO/TiO2-3 are shown in figure 1. The diffraction characteristic peak of GO, RGO and TiO2 indicated in Figure 1. By comparing figure1(a) and (b)-(d), the characteristic peak of GO disappears in RGO at 2θ values of 11.07º, indicating that the GO was reduced after mixed solution adding urea reducing agent[16]. Simultaneously, the characteristic diffraction peak of approximately 25.1º, 37.5º, 48.2º, 54.3º, 62.8º, 69.6º and 75.1º are correspond to the TiO2 structure, which is suggesting that TiO2 nanoparticles are obtained form Ti4+ ions in Ti(SO4)2 solution and with increasing the volume of the urea the intensity of characteristic diffraction peak of TiO2 nanoparticles increase, as shown in figure1.
The FTIR spectra of GO, RGO and RGO/TiO$_2$-2 are shown in figure 2. Figure 2a shows typical absorption bands of GO. The stretching vibrations of the O-H, C=O, C=C and C-OH ring were observed, which correspond to characteristic peak of 3410 cm$^{-1}$, 1727 cm$^{-1}$, 1625.6 cm$^{-1}$ and 1054 cm$^{-1}$, respectively. Figure 2b shows stretching vibrations of the C-OH, C-O epoxy and C-O alkoxy, which correspond to characteristic peak of 1415 cm$^{-1}$, 1223 cm$^{-1}$ and 1054cm$^{-1}$, respectively. Comparing figure 2(a) and figure 2(b), the characteristic peak at 3410 cm$^{-1}$, 1727 cm$^{-1}$, 1625.6 cm$^{-1}$ and 1054 cm$^{-1}$ disappears, indicating that the GO is reduced to RGO. Figure 2c shows typical Ti-O-Ti of RGO/TiO$_2$ characteristic peak between 500 and 1000 cm$^{-1}$[17].

Figure 3 shows FE-SEM images of GO, RGO/TiO$_2$-1 and RGO/TiO$_2$-2. From figure 3a, the sheet of GO is smooth and thin, and sheet of GO has high dispersibility. Figure 3 (b, c and d) show that the mean size of TiO$_2$ nanoparticles has a large distribution ranging from 5 nm to 100 nm. The TiO$_2$ nanoparticles has good interface adhesion with RGO sheets. This may attribute to the Ti$^{4+}$ ions can electrostatic absorption on the surface of GO sheets and under the urea reducing agent the TiO$_2$ nanoparticles was in-situ reduced in RGO sheets. With increase the ratio of urea, the number of TiO$_2$ nanoparticles increase.
The HRTEM and TEM images of RGO/TiO_2-2 are described in figure 4 (a) and (b). 0.352 nm of crystallographic spacing in TiO_2 particle, as illustrated figure 4 (a), correspond with crystallographic plane of (101) of anatase TiO_2. The crumpled RGO sheets are uniformly covered by TiO_2 nanocrystals in the figure 4b, and the grain size of TiO_2 nanoparticles is ranging from 5 nm to 10 nm. At edges of TiO_2 nanoparticles, the thin and semitransparent RGO sheets can be observed.

4. Conclusions
Homogeneous dispersed RGO/TiO_2 nanocomposite was synthesized using precursors of graphene oxide (GO) and Ti (SO_4)_2 and reducing agent of urea solvent by situ hydrothermal reduction method. The results of XRD and FTIR spectra demonstrate that the TiO_2 nanoparticles are tight coupling with RGO sheets. The results of TEM and FESEM images indicate that the grain size of TiO_2 is in the range of 5-10 nm, and TiO_2 homogeneous dispersed in RGO sheets.

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