

Titania nanotube-graphene oxide hybrids with excellent photocatalytic activities

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Abstract: Titania nanotube-graphene oxide (TiO₂ NT-GO) hybrids were prepared by a hydrothermal reaction followed by calcination at different temperatures. Results indicate that flat sheets of GO promote the formation of the TiO₂ NTs. GO is reduced during the hydrothermal and calcination steps, and is inserted into the TiO₂ layers by the interaction between oxygen-containing groups on both the GO and TiO₂. The rates of GO decomposition, GO reduction and TiO₂ NT formation are temperature dependent. The TiO₂ NT-GO hybrid calcined at 350 °C has a high degree of crystallization, a red-shifted absorption and the highest observed photocatalytic activity for the degradation of methylene blue.

Key Words: Nanostructures; Surfaces; Electron microscopy; X-ray photo-emission spectroscopy (XPS); Optical materials

1 Introduction

Titania (TiO₂) is a wide band-gap semiconductor possessing specific chemical properties and a high stability. The band gap of anatase TiO₂ ~3.2 eV enables it photocatalytically active under UV irradiation. Among TiO₂ nanoparticles^[1], TiO₂ nanotubes (TiO₂ NTs) are known to be effective photocatalysts in the degradation of environmental contaminants. TiO₂ NTs have high specific surface areas and improved photocatalytic performances compared with bare TiO₂^[2,3]. TiO₂ NTs can be synthesized via various methods, including electrochemical anodization, sol-gel and hydrothermal methods^[4,5]. In comparison with other techniques, hydrothermal synthesis is an inexpensive and environment-friendly method with the ability to control chemical composition and morphology of the synthesized products. The synthesis conditions affect the phase composition and morphology of hydrothermally synthesized TiO₂.

A series of strategies have been developed to synthesize TiO₂ NT based nanocomposites for the inhibition of high intrinsic electron-hole pair recombination as well as a further modification of the band gap of the composite, such as doping with quantum dots, semiconductors and carbon materials. In particular, there is a growing interest in the combination of carbon based materials and TiO₂ to enhance photocatalytic performance. Graphene is one of the carbon nanomaterials, which is unique and has been intensely studied because of its excellent conductivity and high transmittance^[6,7]. Previous reports have shown that the

addition of graphene improves the supercapacitor performance of MnO₂^[8], photocatalytic performance of ZnO^[9], et al^[10]. Especially, graphene improves the photocatalytic activity of TiO₂^[11, 12], and enhances energy conversion performance in homogeneous and heterogeneous semiconductors, because of its effective electron transfer and interaction effects^[13, 14].

There have been several reports highlighting the improvements in the photocatalytic activity of TiO₂ NT-reduced GO for the degradation of organic molecules and photocatalytic splitting of water. However, TiO₂ nanoparticles tend to agglomerate and have poor interfacial contact with the graphene surface because of the nanoparticle's nearly spherical shape. And their formation process and mechanism is not well elaborated. In this paper, we present a practical hydrothermal reaction technique, in which TiO₂ NTs self-assemble on GO. The self-assembly of TiO₂ NTs on GO leads to a high interfacial contact and offers potential electron-transfer capabilities that improve the photocatalytic properties of TiO₂.

2 Experimental

2.1 Synthesis of GO

GO was synthesized from flake graphite (Pingdu BEISHU Graphite Co. Ltd., Shandong Province, China) using a modified Hummers method^[15]. First, 10 g natural graphite was put in a flask (500 mL), then concentrated sulfuric acid (300 mL) was added slowly while the flask was placed in an ice water bath. After ten min, 45 g

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potassium permanganate was gradually added into the flask over a period of 1 h and the mixture was stirred for another 4 h in the ice water bath. Then 5 wt% H₂O₂ (150 mL) was added within 30 min. The final suspension was filtered to collect solid product that was washed with deionized water until a pH value of 6–7 was obtained. The solid product was dried for 24 h at 80 °C. The resulting graphite oxide product was sonicated for 20 min in distilled water, centrifuged at 4 000 r/min for 20 min to produce a GO aqueous dispersion (0.5 mg/mL). Using this method, we previously showed that the synthesized GO consists of mainly 1–4 layers^[16].

2.2 Synthesis of TiO₂ NT-GO hybrid

38 g NaOH was added to the GO solution (0.5 mg/mL, 62 mL) and heated until the NaOH was dissolved. Rutile-phase TiO₂ was added and after the solution was stirred for 5 min. The resulting solution was poured into a 100 mL Nalgene flask and stored in an oven at 130 °C for 40 h. The resulting dehydrated powder was put in a HCl aqueous solution (0.1 mol/L) for 10 h and washed with distilled water to a Ph value of 6–7. Then the powder was dehydrated and heated at 60 °C for 24 h. The resulting product was named as TiO₂ NT-GO. TiO₂ NT-GO was calcined at different temperatures in a furnace for 1 h at a heating rate of 1 °C/min. Bare TiO₂ NTs were prepared using the same procedure without adding the GO solution.

2.3 Characterization

The structures of the samples were observed using a scanning electron microscope (SEM, Model S4800, Hitachi) and a high-resolution transmission electron microscope (TEM, Model Tecnai G² F20, FEI), at 15±25 kV and 200 kV acceleration voltages, respectively. For the TEM observations, the samples were ultrasonicated in ethanol and then placed on a copper grid. X-ray photoelectron spectroscopic (XPS) measurements were taken using a

Quantum 2000 Scanning ESCA Microprobe (Physical Electronics) using Al K α radiation (1486.6 eV). In the XPS data analysis, peak deconvolution was performed using Gaussian components after a Shirley background subtraction. Solution absorbance was measured using a ultraviolet-visible (UV-vis) spectroscope.

2.4 Spectroscopy and photocatalytic reactions

Photocatalytic degradation of methylene blue (MB) was carried out at ambient temperature in a homemade photocatalytic reactor. The UV-light source was a commercial 8W black-light tube with a spectral peak at 365 nm. 300 mL methylene blue solution (20 mg/L) and 0.05 g photocatalyst were fed into the reactor, then air was blown into the reactor from the bottom via a gas distributor at a flowrate of 4 L/min. After 30 min of premixing, the reactants were irradiated for 80 min. Samples (10 mL), taken before and after irradiation were centrifuged and supernatants were analyzed by recording the absorption peak of methylene blue at 666 nm. The intensity of the main absorption peak was converted to the residual dye concentration (*C*).

3 Results and discussion

Fig. 1 shows the SEM images of the raw material of rutile-phase TiO₂ (Fig. 1a), intermediate product (Fig. 1b) obtained at 130 °C for 20 h through the alkali treatments and acid treatments, and TiO₂ NT-GO hybrid (Fig. 1c). The structure of intermediate product, is markedly different from that of the raw material, more specifically, the nanoparticles present in the raw material are no longer observed and became plate shaped. In Fig. 1c of the TiO₂ NT-GO hybrid, needle-shaped crystals with a length of ~2 μ m were observed in a large amount, which are TiO₂ NTs. After calcination at 550 °C, the TiO₂ NT-GO hybrid is gradually

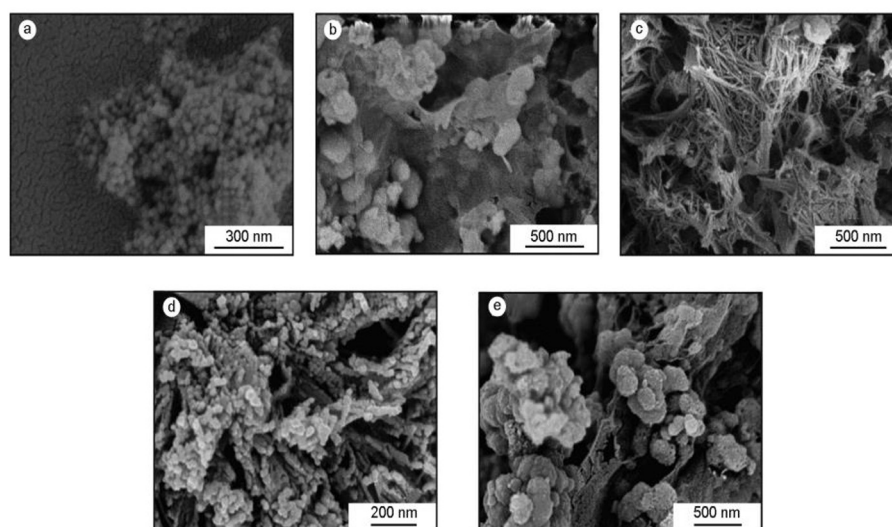


Fig. 1 SEM images of (a) raw material, TiO₂ NT-GO at various reaction time of (b) 20 h and (c) 40 h, (c) TiO₂ NT-GO calcined at 350 °C, and (e) TiO₂ NT-GO sample in which GO solution is without centrifugation

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