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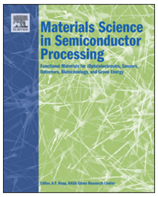

Synthesis and visible catalytic applications of graphene–titania dioxide nanotube composites

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ABSTRACT

A novel photocatalyst of graphene–titania dioxide nanotube (GN–TNT) composites was prepared using a simple hydrothermal reaction with ascorbic acid as a reducing agent. High resolution transmission electron microscope (HR-TEM), fourier transform infrared spectrometer (FT-IR), thermo gravimetric analyzer (TGA) and N_2 adsorption/desorption analyzer (BET) methods were used to assess the morphologies and structures of as-synthesized materials. HR-TEM analysis further confirmed the presences of graphene and titanium (TiO_2) nanotubes in the nanocomposite photocatalyst. The results exhibited that photocatalytic performance of a GN–TNT photocatalyst significantly improved under visible light. In addition, the existence of a competitive effect between As^{3+} and reactive black 5 (RBK5) molecules in the mixed solution was found. The photocatalytic process is also discussed in this paper.

1. Introduction

Titanium dioxide (TiO_2) is commonly used as the photocatalytic material in the field of water treatment; its photocatalytic properties have attracted much interest because of its great capacity for oxidation, wide band, nontoxicity, low cost, widespread availability, and long-term stability [1]. Under UV light, electrons in TiO_2 are excited from the valence band (VB) to the conduction band (CB), creating electron–hole pairs that react with pollutants in order to remove them [2,3]. The electron–hole pairs are mainly responsible for the photocatalytic activity. However, the faster recombination rates of photogenerated electron–hole pairs and the limited response from ultraviolet light greatly hinder its application in the field of photocatalysis. To address these issues, great efforts have been expended in numerous applications, for example, noble metal deposition [4,5], compound semiconductors [6,7], ion doping [8,9] and so on. However, these methods only improved the photocatalytic efficiency to a limited extent, while utilizing UV light, rather than visible light [10]. This study is focused upon solving these problems.

Similar to TiO_2 nanoparticles, TiO_2 nanotubes were modified products of TiO_2 particles, and their specific surface area increased significantly compared with TiO_2 particles. Larger specific surface area of these materials can improve pollution molecule adsorption and degradation. Therefore, theoretically, TiO_2 nanotubes have better potential to adsorb and degrade pollutants than TiO_2 particles.

Graphene (GN) has moved to the forefront of material science, since its first preparation in 2004 [11]. Due to its unique planar structure, excellent transparency, superior electron conductivity and mobility, high specific surface area, and high chemical stability, GN is regarded as an

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ideal, high performance candidate to prepare GN-based nanocomposites for energy storage and conversion [12–15]. For example, nanocomposites of titanium oxide (TiO_2) and reduced graphene oxide (RGO) were successfully prepared by the hydrothermal method; the TiO_2–GO composite demonstrated excellent photocatalytic activity, however, its application was limited to the UV light range only [16].

In this study, a novel photocatalyst of GN–TNT nanocomposites was synthesized through a simple hydrothermal reaction with ascorbic acid as a reducing agent. The addition of ascorbic acid has helped to revert graphene oxide (GO) to graphene (GN) [17]. GO was prepared by a modified Hummers Method and reduction was achieved during hydrothermal synthesis. Material properties were characterized by HR-TEM, DFM, FT-IR, and XRD. In order to explore the photocatalytic properties of GN–TNT composites, the study of removing RBK5 dye and As^{3+} ions in solution under visible light were conducted; different ratios of RBK5 dye to As^{3+} ions are further discussed forthcoming.

2. Experiment

2.1. Chemicals and materials

The TiO_2 used in this study was Degussa P25 (ca. 80% anatase and 20% rutile) with a BET surface area of $\sim 50\ m^2\ g^{-1}$. Graphite flake (natural, −325 mesh) with a purity of 99.8% was purchased from Alfa Aesar. Ascrobic acid was supplied by Colnbrook Bucks England. All chemicals were of analytical grade and used as received.

2.2. Synthesis of TNT

TNT was synthesized using the hydrothermal method. First, 5.0 g of P25 was dispersed into 10 M of NaOH aqueous solution. The suspension was then transferred into a Teflon-lined stainless steel autoclave before being stirred for 60 min and heated at 135 °C for 72 h. The white powder obtained was then washed and filled with deionized water and 0.1 M HNO_3 three times. The products were then dried at 110 °C. The final products were calcined at 400 °C. In order to maintain the fineness of the powder, the prepared TNT was ground and sieved (200 mesh).

2.3. Synthesis of GN–TNT nanocomposite

GO was prepared according to the modified Hummers Method [18–20]. The GN–TNT composite was prepared using a hydrothermal treatment process. Ascrobic acid was used as the reducing agent. First, 0.1 g of GO was added to 200 mL of deionized water and subjected to ultrasonic dispersion to obtain a homogeneous GO dispersion. Then, 2 g of TNT and 0.05 g of ascrobic acid were added to the GO dispersion. The mixture was then transferred to a Teflon-lined stainless steel autoclave and reacted at 120 °C for 4 h. The product was then washed with deionized water and dried at 50 °C.

2.4. Characterization

Sample morphology was characterized by high resolution transmission electron microscopy (HR-TEM; JEOL inc., EM2100) and a dynamic force microscope (DFM, Seiko Instruments Inc., SPA-300HV). The structure of the samples was measured by a Fourier-transform infrared spectra analyzer (FT-IR; Thermo Scientific inc., NICOLET iS10), X-ray diffraction (XRD; Rigaku inc., Ultima IV), and a N_2 adsorption–desorption isotherm analyzer (Brunauer–Emmett–Teller (BET) specific area). The optical adsorption properties of the samples were investigated using a UV spectrometer (UV–vis; Hitachi inc., U-3900).

2.5. Photocatalytic experiments

Photocatalytic activities of the photocatalysts were measured by degrading RBK5 dye and As^{3+} ions in an annular quartz glass tube. 150 W visible light lamp ($\lambda = 400$ nm) was used as the light source. 0.4 g of photocatalyst was added to 1 L mixed solution with different initial concentrations of As^{3+} and RBK5 dye. Prior to irradiation, the suspensions were magnetically stirred in dark for 60 min to reach adsorption–desorption equilibrium. The concentration of RBK5 dyes and As^{3+} ions was determined by a UV–vis spectrophotometer at 600 nm and microwave plasma atomic emission spectroscopy (MP-AES, Agilent 4100), respectively.

3. Results and discussion

3.1. Morphologies and microstructures of the as-synthesized materials

In order to certify the successful preparation of GN–TNT photocatalysts and GO sheets, the morphologies and microstructures of materials were observed via DFM and HR-TEM, as shown in Fig. 1. The DFM picture shown in Fig. 1(a) indicates that the thickness of the GO sheets prepared in this study were ~2 nm, which is consistent with the results in the literature [21]. Fig. 1(b) and (c) show that TNT prepared in this study had a tubular structure with an average diameter of 8 nm. Furthermore, obvious wrinkles are observable in Fig. 1(b), which fully confirms the formation of graphene sheets. EDX analysis of GN–TNT composites is shown in Fig. 1(d). The GN–TNT photocatalyst contained Ti, O and C. Additionally, the presence of Cu was attributed to the copper which carry samples.

3.2. Structures and properties of the as-synthesized materials

The structure and functional groups of the materials was investigated through the FTIR spectra analysis, as shown in Fig. 2(a). The FT-IR spectrum of TiO_2 was very similar to TNT, which indicated that the modification of TiO_2 did not change the original structure and functional groups and only changed the morphologies. GO spectra showed adsorption bands for the carboxyl C=O ($1723\ cm^{-1}$), aromatic C=C ($1621\ cm^{-1}$), epoxy C–O ($1220\ cm^{-1}$), alkoxy C–O ($1043\ cm^{-1}$), and hydroxy OH