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Three-dimensional titanate–Graphene oxide composite gel with enhanced photocatalytic activity synthesized from nanofiber networks

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ABSTRACT

We report the synthesis of a novel three-dimensional titanate–graphene oxide (TiGO) composite gel with controllable morphology through a facile one-pot solvothermal approach. This technique directly utilizes tetra-butyl titanate as a titanium source and acetic acid (HAc) as a stabilizer and cross-linking agent. Gel formation at the macro level and morphological evolution of flower-like networks into nanofibers at the micro level were controlled by regulating the amounts of graphene oxide (GO) and HAc added to the reaction system. TiGO composite is composed of nanofiber bundles and its photocatalytic activity was evaluated by photocatalytic decolorization of methyl orange aqueous solution under UV irradiation. The improved photocatalytic performance was attributed mainly to synergistic effects of titanate and GO.

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1. Introduction

Graphene oxide (GO) is widely used as a unique building block in different supramolecular interactions, such as hydrogen bonding, coordination, electrostatic interaction, and π–π stacking assembly, for 3D hydrogel structure formation [1–5]. Three-dimensional networks based on GO sheets exhibit higher mechanical strength, higher specific surface area, better electrical conductivities, and improved thermal, chemical, and electrochemical stability than 2D GO nanosheets. Previous reports showed that 2D GO nanosheets easily form into irreversible agglomerates or restack into graphitic structures, thereby significantly reducing the accessible surface area and deteriorating the actual performance [6,7]. As such, individual 2D GO nanosheets were integrated into 3D macroscopic structures, such as porous films, scaffolds, and networks, to obtain high-performance graphene-based materials for practical monolithic applications. Gelation, a main strategy for construction of 3D GO, was developed to facilitate the formulation of high-performance graphene materials with a wide range of practical applications [8–12].

To date, GO-based functional materials are fabricated through various processes, such as solution mixing [13], in situ growth [14], impregnation [15,16], hydrothermal, and/or solvothermal methods [17,18]. Solvothermal method is an effective and reliable method used to produce 3D GO-based gel because of its stable reaction condition and easy adjustment of microstructure and properties by changing the concentration of the GO dispersion and solvothermal reaction time. A GO sheet can be recognized as a single-layered graphite bearing various hydrophilic oxygenated functional groups [19]. Thus, various small molecules, polymers, or ions can promote the gelation of GO through different supramolecular interactions even at very low GO concentrations [20–23]. For example, Bai et al. [24] demonstrated the preparation of GO-conducting polymer composite hydrogels via in situ polymerization of aromatic monomers in GO dispersions; the resulting hydrogels exhibited high conductivities and electrochemical activities and could be used to fabricate highly sensitive ammonia sensors. Tang et al. [25] showed that noble metals (e.g., Au, Ag, Pd, Ir, Rh, Pt, etc.) promoted the assembly of GO into macroscopic porous structures; the authors found that combination of noble-metal nanocrystals and GO layers result in excellent Heck reaction catalytic activity and selectivity. The applications of graphene-based materials in energy, environment, sensing, and biological fields often require 2D graphene sheet assembly into 3D architectures [26–29]. As such,

the unique properties of graphene-based materials must be maximized for their practical applications. Inorganic nanomaterial GO composite, as an important member of functionalized GO materials, exhibits a myriad of potential applications [15,18,30,31]. The integration of nanostructured materials into macroscopic devices, which can translate phenomena at the nanoscale to the macroscopic level, is a vital aspect for applications of nanomaterials. Studies have reported on GO-based gels, but the use of excellent photocatalytic properties of titanate has been rarely investigated; titanate is used to construct 3D TiGO composite gel for degradation of organic contaminants in liquid phase.

Considering this observation, we fabricated a novel 3D TiGO composite gel with controllable morphology through a one-pot solvothermal approach. The photocatalytic performance of the resultant product was investigated. Mechanisms underlying the formation of TiGO composite gels were also studied. Macrolevel gel formation and microlevel flower-like nanofiber morphological evolution can be controlled by regulating GO and HAc concentrations in the reaction system. The photocatalytic performance of the TiGO composites is seriously affected by the GO/tetrabutyl titanate (TBT) ratio. In this monolithic structure, the large surface area and unique 3D structure of the TiGO nanocomposites can offer numerous active adsorption sites and photocatalytic reaction centers. The resulting 3D TiGO composite gel displays the synergistic effects of the assembled Ti and GO, displaying improved photocatalytic performance, including high photocatalytic activity and good photocatalytic stability and reusability.

2. Experimental section

2.1. Chemicals

Graphite powder, phosphorus pentoxide (P_2O_5, 98%), potassium persulfate ($K_2S_2O_8$, 99.5%), acetic acid (HAc, 99.5%), and potassium permanganate ($KMnO_4$) were obtained from Tianjin Kermel Chemical Co., Ltd. (China). TBT and aqueous hydrogen peroxide solution (H_2O_2, 30%) were obtained from Sinopharm Chemical Co., Ltd. (China). All of the reagents were of analytical grade and used without further purification.

2.2. Synthesis of GO

GO was synthesized from expanded graphite powder using a modified Hummers method [32,33]. This two-step synthetic technique began with pre-oxidation. Briefly, 3.0 g of graphite was added to a mixture of 30 mL of 98% H_2SO_4 with 3 g each of $K_2S_2O_8$ and P_2O_5. The solution was sonicated for 5 min, placed in an oil bath, heated to 80 °C, and then stirred for 6 h. The product was subsequently diluted with 500 mL of deionized water, filtered through a 0.2 μm nylon film, and dried under ambient conditions. The product obtained from this first step was used for the second step, i.e., oxidation. Exactly 150 mL of 98% H_2SO_4 and 20 mL of 85.0% H_3PO_4 were added slowly to the obtained product with stirring over an ice water bath. Then, 18 g of $KMnO_4$ was gradually added to the mixture with stirring for 4 h at 20 °C. The mixture was removed from the ice bath and subsequently stirred for another 8 h at 35 °C. Addition of 1000 mL of distilled water and 24 mL of 30% H_2O_2 solution terminated the reaction. Finally, the GO was obtained through filtration, ultrasonication, and vacuum drying.

2.3. Synthesis of TiGO composite gel

In a typical synthesis, 36.75 mL (V_1) of HAc was kept under static conditions for 0.5 h at 40 °C. After heating, 1 mL of TBT was added dropwise to the HAc with continuous stirring. The resulting white suspension was stirred for 24 h at 350 rpm and 40 °C. To produce the GO dispersions, 6 mg of GO was mixed with 10 mL (V_2) of HAc solution by sonicating for 0.5 h. The GO dispersions were added to the white suspension obtained previously and stirred for 2 h at 40 °C. Finally, the solutions were placed in a Teflon-lined stainless-steel autoclave for 24 h at 150 °C. After cooling to room temperature, the products were retrieved. Five composite gel samples with varying GO weights were synthesized and designated as TiGOx (i.e., samples to which 0, 6, 12, 18, and 24 mg of GO were added were designated TiGO0, TiGO1, TiGO2, TiGO3, and TiGO4, respectively). Another set of composite gel samples with varying HAc V_2 and only 6 mg of GO were also prepared (i.e., samples to which 5, 10, 20, 30, and 40 mL of HAc were added were designated as TiGOA1, TiGOA2, TiGOA3, TiGOA4, and TiGOA5, respectively).

2.4. Characterization

To determine the phase purity and crystal structure of the samples, X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance X-ray diffractometer (40 kV, 40 mA) using Cu Kα (λ = 0.15406 nm) radiation. The data were collected from 5° to 80° (2θ) with a resolution step size of 0.1° s^{-1}. Raman measurements were recorded on a JY Lab-Ram HR800 spectrometer with a 488 nm Ar$^+$ ion laser. Thermogravimetric analysis (TGA) was carried out on a TGA1500 DSP-SP instrument at a heating rate of 20 °C min^{-1} from room temperature to 800 °C under an air atmosphere. To observe the morphologies of the prepared TiGOx and TiGOAx samples, high-resolution transmission electron microscopy (HRTEM) was performed using a JEM-2100 electron microscope with an acceleration voltage of 200 kV. The sample powder was dispersed in ethanol by sonication, dropped onto a copper grid, and air-dried. Field emission scanning electron microscopy (FESEM) micrographs of samples were obtained by a Nova NanoSEM 450 microscope operated at an acceleration voltage of 10.0 kV. Sample powder was dispersed in ethanol, dropped onto the surface of a silicon wafer, and then sputter-coated for two cycles with gold to avoid charging under the electron beam prior to examination. UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded on a SHIMADZU UV-2600 spectrophotometer. The specific surface areas of freeze-dried gels were measured on TriStar 3020 Surface Area and Porosity Analyzer and calculated by Brunauer-Emmett-Teller (BET) method. Samples were degassed for 6 h at 180 °C before measurements. Fourier transform infrared (FT-IR) spectra were recorded on an IRPrestige-21 spectrometer with a resolution of 4 cm^{-1} and a scan number of 32 by using compressed KBr pellets containing 1 wt% of the sample. Sample composition was determined using X-ray photoelectron spectroscopy (XPS) on a ESCALAB 250 spectrometer with a monochromatic Mg Ka X-ray source.

2.5. Photocatalytic activity

Methyl orange (MO) photodegdradation was performed in an aqueous solution under UV light irradiation at room temperature. The reaction was conducted in a cylindrical quartz reactor with a water circulation feature on its outer wall. A 375 W high-pressure mercury lamp was used as the UV light source, and the reactant–light source distance was 20 cm. To test photocatalysis, 1.5 g of the undried gel (containing 1.48 g of HAc) was mixed with 100 mL of MO solution (30 mg L^{-1}) with stirring. Prior to irradiation, the mixture was placed in the dark for 0.5 h to achieve the adsorption–desorption equilibrium. The absorbance of the target organic compounds was constant over time, indicating that the adsorption–desorption equilibrium was reached [34]. Subsequently, the solution was illuminated with UV lamp and bubbled with oxygen at a constant flow rate. To determine change in MO solution concentration during UV irradiation, 10 mL of the solution was obtained at 0.5 h intervals. The absorbance of the correspond-