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Immobilization of TiO_2 nanofibers on reduced graphene sheets: Novel strategy in electrospinning

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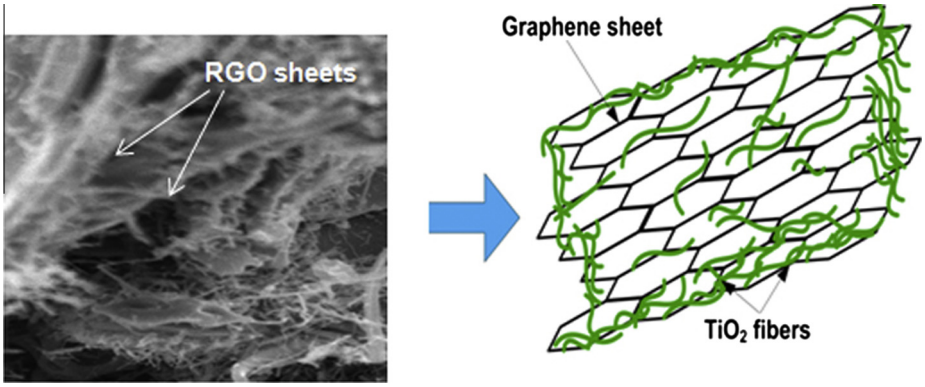
GRAPHICAL ABSTRACT



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ABSTRACT

A simple and efficient approach is developed to immobilize TiO_2 nanofibers onto reduced graphene oxide (RGO) sheets. Here, TiO_2 nanofiber-intercalated RGO sheets are readily produced by two-step procedure involving the use of electrospinning process to fabricate TiO_2 precursor containing polymeric fibers on the surface of GO sheets, followed by simultaneous TiO_2 nanofibers formation and GO reduction by calcinations. GO sheets deposited on the collector during electrospinning/electrospray can act as substrate on to which TiO_2 precursor containing polymer nanofibers can be deposited which give TiO_2 NFs doped RGO sheets on calcinations. Formation of corrugated structure cavities of graphene sheets decorated with TiO_2 nanofibers on their surface demonstrates that our method constitutes an alternative top-down strategy toward fabricating verities of nanofiber-decorated graphene sheets. It was found that the synthesized TiO_2/RGO composite revealed a remarkable increased in photocatalytic activity compared to pristine TiO_2 nanofibers. Therefore, engineering of TiO_2 nanofiber-intercalated RGO sheets using proposed facile technique can be considered a promising method for catalytic and other applications.

1. Introduction

Fabrication of graphene-based semiconductor nanocomposites has attracted considerable attention in recent years because of

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their unique physicochemical properties [1–3]. The excellent electron conductivity and high transparency with its two-dimensional plate-like structure, graphene-based semiconductor materials can easily enhance the catalytic, electrical, optical, thermal, and mechanical properties of the composite [4–6].

TiO_2 is a typical semiconductor with high chemical stability, strong photocatalytic activity, and good photoelectric performance [7], reported in various types of nanostructures (e.g., nanoparticles [7], nanotubes [8], nanowires [9], nanosheets [10], and nanofibers [11]). However, the photocatalytic activity of TiO_2 is limited by its wide band gap energy (3.0 and 3.2 eV for rutile, and anatase phase, respectively), which renders its capacity under only UV light [12]. Moreover, instantaneous recombination of radiation-induced electron–hole (e–h) pair leads to decrease the efficiency in the photocatalytic activity of TiO_2. Therefore, a number of strategies to fabricate composite TiO_2 nanostructures have been proposed to challenge these limitations[13].

Notably, resent research works, as reported in literature, are inclined to emphasize the enhanced photocatalytic activity of TiO_2 by doping them on graphene sheets. The reported methods to fabricate graphene–TiO_2 hybrids involved either mixing a GO dispersion and TiO_2 precursors, followed by reduction [14,15] or direct interaction of NPs with GO dispersion to get NPs decorated RGO sheets during hydrothermal treatment [16,17]. First method requires reducing agents which are mostly toxic whereas second one may not provide well attached particles on RGO sheets. Formation of effectively doped TiO_2 particles on graphene sheets without using toxic reducing reagent is an important aspect for the formation of stable composite. Furthermore, deposition of TiO_2 nanofibers (NFs) on the surface of RGO sheets might be more effective than that of NPs doped RGO sheets. It is reported that the photocatalytic activity of TiO_2 NFs is better than that of TiO_2 NPs [11]. Therefore, our knowledge regarding the specific advantage of NFs over NPs on how to design efficient TiO_2 NFs decorated RGO sheets to enhance its photocatalytic performance is reported in this work. Our experience regarding the fabrication of GO/polymer electrospun fibers [18,19] indicates that extremely small size GO sheets can only be incorporated through NFs and most of the GO sheets in electrospun mats are in micro-sized (deposited by electrospatay), which are covered with a large number of NFs throughout the mat. Therefore, we are motivated to grow TiO_2 NFs on the surface of these large GO sheets. Here, we describe the result of an investigation that has led to the development of a new versatile approach for the fabrication of TiO_2 NFs decorated RGO sheets using electrospinning followed by calcinations. Importantly, this two steps procedure does not require the use of toxic reducing agent for the reduction of GO, where precursor containing polymer fibers on GO sheets simultaneously produce TiO_2 NFs-intercalated RGO sheets on calcinations.

2. Experimental

2.1. Materials

Synthetic graphite (lateral size <20 μm), potassium permanganate, sulfuric acid, hydrogen peroxide, titanium isopropoxide (TiP), polyvinyl acetate (PVAc, Mw = 500,000) were purchased from Sigma Aldrich and used as-received.

2.2. Synthesis of graphene oxide (GO)

GO was prepared using modified Hummer's method [20] according to our previous work [21]where three-neck flask containing 250 ml H_2SO_4 and 10 g graphite was kept in an ice bath for 15 min at low temperature (<5 °C) followed by addition of 35 g of $KMnO_4$ with continuous stirring for 5 h. The mixture was cooled in an ice bath followed by the addition of 500 ml distilled water. Excess aqueous H_2O_2 (30%) was added to this mixture until the color changed to a brilliant yellow. After the mixture was allowed to settle, the clear supernatant was decanted and the sediment was washed repeatedly with distilled water until supernatant become neutral. The air dried powder was kept in a vacuum oven for 2 days at 65 °C before using for composite synthesis.

2.3. Fabrication of TiO_2 NFs-intercalated RGO sheets

The fabrication process of TiO_2/RGO composite is illustrated in scheme 1. Here, different amounts of homogeneous GO dispersion (10, 20, 50 and 100 mg of as-synthesized GO in 1 g DMF, 1 h sonication) was mixed with TiO_2 precursor containing PVAc solution. TiO_2 precursor containing PVAc solution was prepared by mixing 6 g of PVAc solution (18 wt%) and 5 g of clear solution of titanium isopropoxide (TiP) (obtained by drop wise addition of acetic acid with continuous stirring). Electrospinning was carried out at room condition where the parameters include 18 kV applied voltage, tip-to-collector distance of 15 cm, and solution feed rate of 1 ml/h. Similar electrospinning solution without GO was used to prepare pristine TiO_2 NFs. Dried electrospun mats were treated in air at 500 °C for 2 h.

2.4. Chatacterization

Morphology of electrospun composite membrane and calcined TiO_2 and TiO_2/RGO composite was observed using scanning electron microscope (JEOL Ltd., Japan) and transmission electron microscope (TEM, JEM-2010, JEOL, Japan). Information about the phase and crystallinity was obtained with a Rigaku X-ray diffractometer (XRD, Rigaku, Japan) with Cu Kα (λ = 1.540 Å) radiation over Bragg angles ranging from 10° to 80°. Infrared spectra and Raman spectra of samples were recorded by using an ABB Bomen MB100 spectrometer (Bomen, Canada) and FT-Raman spectroscopy (RFS-100S, Bruker, Germany), respectively. Room temperature photoluminescence (PL) spectrum was recorded by Perkin Elmer Instruments. The photocatalytic activity of the TiO_2-doped RGO nanosheets with different content of GO was evaluated by observing the degradation of rhodamine B (RhB) dye solution and compared with the pristine TiO_2 and commercial P25. The process was carried out in a Petri dish which was equipped with a ultra-violet lamp (λ = 365 nm). The distance between Petri dish and UV lamp was 5 cm. In each case, 25 ml of dye solution (10 ppm concentration) and 20 mg catalyst were mixed to make suspension by stirring. At specific time intervals, 1 ml of the sample was withdrawn from the system and centrifuged to separate the residual catalyst, and then the absorbance intensity was measured at the corresponding wavelength. The reusability of the synthesized photocatalyst was evaluated upto three cycles under identical conditions.

3. Results and discussion

The morphology of TiP/PVAc composite fibers before and after calcinations was shown in Fig. 1, which shows that continuous smooth TiO_2 NFs are formed after calcinations. SEM image of GO containing composite fibrous mat (Fig. 2a) clearly shows the presence of GO sheets which are distributed throughout the mat (composite mat without GO has no any sheet like structure (Fig. 1a). The GO sheets are in micro-sized and they are highly interconnected with TiO_2 NFs (Fig. 3b). TEM image also revealed that large GO sheets were present with numerous fibers (Fig. 3c). When electrospun NFs with large GO sheets were deposited on