



Facile synthesis of reduced graphene oxide/titania composite hollow microspheres based on sonication-assisted interfacial self-assembly of tiny graphene oxide sheets and the photocatalytic property



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ABSTRACT

Sonication-assisted interfacial self-assembly of tiny GO sheets (whose lateral size less than 200 nm) on cationic polyelectrolyte-decorated SiO₂ microspheres was achieved, leading to the formation of uniform GO thin layer coated SiO₂ microspheres (i.e., SiO₂/GO composite microspheres), which possessed high aqueous dispersity. RGO/TiO₂ composite hollow microspheres were further one-pot synthesized by solvothermal treatment of SiO₂/GO microspheres in the presence of polyvinylpyrrolidone (PVP) using TiF₄ as Ti precursor and ethanol/water as a mixed solvent. It was found that PVP and appropriate volume ratio of ethanol to water (v/v = 20:8) were key factors for the fabrication of RGO/TiO₂ hollow microspheres with well-defined microspherical hollow structure. The composition, morphology, structure and crystalline phase of RGO/TiO₂ hollow microspheres were carefully examined by a series of characterizations like FTIR, UV–vis and Raman spectroscopy as well as XRD, SEM and TEM inspections. Compared with the solvothermally synthesized TiO₂ hollow microspheres and blended RGO–TiO₂ hollow microspheres, RGO/TiO₂ hollow microspheres displayed rather enhanced photocatalytic performance toward the degradation of methylene blue. Moreover, RGO/TiO₂ hollow microspheres were durable and robust enough so that they were able to be reused for many times with only a little loss of photocatalytic activity and without the destruction of morphology and structure, exhibiting prominent application potential. This work reveals a facile and versatile synthetic methodology for the fabrication of advanced GO- and RGO-containing hybrid materials with unique shapes and designed properties.

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1. Introduction

Titania (TiO₂), as a promising semiconductor photocatalyst, has received ongoing attention due to its chemical inertness, resistance to photocorrosion, low-cost, nontoxicity and earth abundance. These excellent physical and chemical properties make it one of the most employed materials in various traditional and emerging applications such as photocatalytic water-splitting, self-cleaning, pigments, cosmetics, sensors, batteries and so on [1–3]. It has been known that the photocatalytic activity of TiO₂ depends on the particle size, structure, crystallographic phase, crystallinity, specific surface area and composition [3–5]. As a consequence, lots of

studies with respect to tuning these factors to improve or optimize the photocatalytic performances of TiO₂ matters were widely reported [4–14]. For instance, by means of construction of unique morphologies, generation of heterogeneous structures, deposition of noble metal nanoparticles, doping with inorganic ions as well as hybridization with carbonaceous species and other metaloxides, the resultant TiO₂-based materials often exhibit photocatalytic enhancement to a large extent [4–14]. Among these approaches, the combination of TiO₂ with reduced graphene oxide (RGO) has especially attracted much interest in recent years [12–14]. Because RGO not only facilitates the charge transfer of electrons to prolong the separation of photogenerated electrons and holes, but also increases the adsorption of substrate molecules on catalysts via π – π interactions, leading to superior photocatalytic efficiency of the final RGO/TiO₂ composites [12,13].

In general, relying on the large surface area of graphene oxide (GO) sheets, the fabrication of RGO/TiO₂ composite materials was achieved by introducing TiO₂ nanoparticles on GO sheets followed

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by chemical, photochemical or hydrothermal reduction of the GO component to RGO [14–19]. In this way, GO sheets were utilized as supports, while TiO_2 nanoparticles were grown or deposited as guest substances, giving rise to unitarily structural features of the synthesized RGO/ TiO_2 hybrid materials [14–19]. To overcome this disadvantage and develop RGO/ TiO_2 composites with multiple structures, hybridization of RGO with TiO_2 species, which possessed different morphologies, was conducted as well [5,12,13,20–24]. For example, by mixing aqueous dispersions of GO sheets with those of surface-aminated TiO_2 microspheres and egg-like TiO_2 hollow particles, respectively, the corresponding GO/ TiO_2 hybrids were produced, which were subsequently converted into RGO/ TiO_2 composites after hydrothermal reduction of the outer GO layer to RGO and further thermal annealing [13,20]. Similarly, TiO_2 nanoparticles were composited with GO sheets, and then the incorporated TiO_2 nanoparticles were transformed to $\text{Na}_2\text{Ti}_3\text{O}_7$ nanofibers after hydrothermal treatment in the presence of NaOH [21]. Such GO/ $\text{Na}_2\text{Ti}_3\text{O}_7$ intermediate underwent acidification and carbonization in inert atmosphere to give nanofibrous RGO/ TiO_2 hybrid material [21]. In addition, GO sheets were deposited on highly ordered TiO_2 nanotube arrays, and the loaded GO films were thermally, hydrothermally or electrochemically reduced to RGO, yielding nanotubular RGO/ TiO_2 composites [22–24]. Three-dimensional (3D) TiO_2 hollow microspheres were also pre-synthesized, and then its aqueous suspension was solvothermally treated in the presence of GO sheets, poly(L-lysine) and ethanoldethylene glycol, resulting in the formation of 3D structured RGO/ TiO_2 composite material [5]. Unfortunately, these strategies mostly suffer from tedious synthetic procedures including preparation and surface modification of TiO_2 materials, hybridization of TiO_2 with GO sheets, reduction of GO component within the intermediate products, high-temperature crystallization of the combined TiO_2 as well as long reaction time and rigorous reaction condition, hence severely hindering their application potential. Therefore, it is of great importance and urgency to develop a facile, mild and economic approach to achieve the fabrication of RGO/ TiO_2 composites with distinct structures and morphologies. Thanks to the intrinsic fascinating characteristics of GO like splendid aqueous dispersity, abundant oxygen-containing groups, negatively charged nature and excellent flexibility, the interfacial self-assembly of GO sheets has recently been demonstrated to be a versatile technique to construct novel GO- and RGO-based materials and devices [25–29]. In the present work, we made full use of this methodology and realized the self-assembly of tiny GO sheets on cationic polyelectrolyte-decorated SiO_2 colloidal microspheres with the aid of intense sonication, yielding GO thin layer wrapped SiO_2 microspheres. The resultant SiO_2 /GO composite microspheres were sequentially subjected to solvothermal treatment in the presence of polyvinylpyrrolidone employing TiF_4 as Ti precursor and ethanol/water as a mixed solvent. During the solvothermal process, the deposition, growth and crystallization of TiO_2 nanoparticles on substrate microspheres, the reduction of GO coating to RGO and the removal of the inner SiO_2 core were simultaneously accomplished in one pot. As such, RGO/ TiO_2 composite hollow microspheres were conveniently synthesized (Fig. 1), which displayed excellent photocatalytic performance toward the degradation of methylene blue in aqueous media.

2. Experimental

2.1. Reagents and materials

Tiny GO sheets with the lateral size less than 200 nm were provided by Nanjing JCNANO Technology CO., Ltd. (Nanjing, China). Poly(diallyldimethylammonium) chloride (PDDA) with average

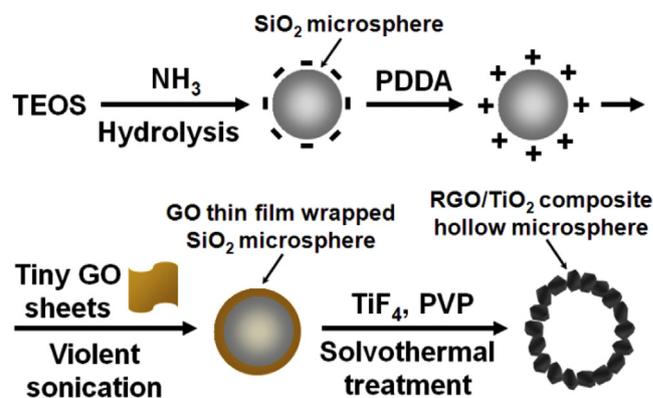


Fig. 1. Schematic illustration of synthesis of RGO/ TiO_2 composite hollow microspheres.

molecular weight of 200,000–350,000, polyvinylpyrrolidone (PVP) with average molecular weight of 40,000, tetraethyl orthosilicate (TEOS), commercial TiO_2 powder (Degussa P25) and TiF_4 were purchased from Sigma–Aldrich CO. Ltd. Milli-Q water (resistivity, 18.2 $\text{M}\Omega\text{ cm}$) was used throughout the work. All other chemicals were guaranteed reagents and used without further purification.

2.2. Synthesis of SiO_2 colloidal microspheres

SiO_2 colloidal microspheres were prepared according to a modified Stöber method [30,31]. Typically, 100 mL of ethanolic solution containing 0.04 mol TEOS was rapidly mixed with another 100 mL of ethanolic solution containing 0.12 mol ammonia and 3.4 mol water. The resulting mixture was allowed to react overnight under moderate stirring to give white SiO_2 colloidal microspheres, which were harvested by centrifugation, washing and drying.

2.3. Synthesis of PDDA-decorated SiO_2 microspheres

1.2 g of SiO_2 microspheres were ultrasonically dispersed in 120 mL water. Then, such 120 mL of aqueous suspension of SiO_2 microspheres was dropwise added into 100 mL of aqueous solution containing 1.2 g PDDA under sonication. After vigorously stirring the resulting mixture for 24 h, the positively charged SiO_2 microspheres (i.e., the PDDA-decorated SiO_2 microspheres) were produced, which were separated by centrifugation. Finally, they were dried and collected after several washing–centrifugation cycles.

2.4. Synthesis of SiO_2 /GO composite microspheres

100 mg of tiny GO sheets were dispersed in 200 mL of water with the help of sonication for 45 min to form an aqueous GO suspension. Subsequently, it was centrifugated at the speed of 16000 rpm for 5 min to get rid of any aggregates and the resulting upper GO suspension was collected and used for the following sonication-assisted self-assembly process. 125 mL of the pretreated GO suspension and 125 mL of aqueous suspension of PDDA-decorated SiO_2 microspheres (4 mg mL^{-1}) were respectively sonicated for 30 min to ensure the homogeneousness. Then, the above aqueous suspension of PDDA-decorated SiO_2 microspheres was slowly dropped into the pretreated aqueous GO suspension under intense sonication (160 W) within 30 min. The resulting mixture was continuously sonicated for another 30 min to complete the interfacial self-assembly of tiny GO sheets on the positively charged SiO_2 microspheres, thus yielding GO encapsulated SiO_2 microspheres (i.e., the SiO_2 /GO composite microspheres). Afterwards, they were separated from the unreacted tiny GO sheets by

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