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Synthesis and characterization of nitrogen-doped TiO_2 coatings on reduced graphene oxide for enhancing the visible light photocatalytic activity

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ABSTRACT

Nitrogen-doped TiO_2 coatings on reduced graphene oxide were prepared *via* a sonochemical synthesis and hydrothermal process. The nanocomposites showed improved photocatalytic activity due to their large specific surface areas (185–447 m^2/g), the presence of TiO_2 in the anatase phase, and a quenched photoluminescence peak. In particular, GN3-TiO_2 (nitrogen-doped TiO_2 coatings on rGO with 3 ml of titanium (IV) isopropoxide) exhibited the best photocatalytic efficiency and degradation rate among the materials prepared. With nitrogen-doped on the reduced graphene oxide surface, the photocatalytic activity is enhanced approximately 17.8 times compared to that of the pristine TiO_2. The dramatic enhancement of activity is attributed to the nitrogen contents and rGO effectively promoting charge-separation efficiency and providing abundant catalytically active sites to enhance the reactivity. The composites also showed improved pollutant adsorption capacity, electron–hole pair lifetime, light absorption capability, and absorbance of visible light.

1. Introduction

Photocatalysis, an advanced oxidation technology (AOT), has excellent potential owing to its attractive low-temperature, non-energy intensive approach, and ability to rapidly degrade a wide range of non-biodegradable pollutants in applications such as chemical waste remediation and solar energy conversion. Semiconductor-mediated photocatalytic reactions are an efficient method for environmental detoxification, facilitating the conversion of toxic organic pollutants into carbon dioxide and water [1–5]. Titania (TiO_2) has emerged as the most promising photocatalyst due to its cost effectiveness, environmental compatibility, biological and chemical inertness, and long-term stability [6,7]. Nevertheless, TiO_2 still has some disadvantages that significantly reduce its photocatalytic efficiency, including a wide band gap and fast recombination of photogenerated electron–hole pairs [8,9]. Since UV light is known to account for only a small fraction (8%) of solar light relative to visible light (45%), numerous attempts have been made to improve photocatalytic performance in the visible region [10–15]. Several strategies to modify photocatalytic efficiency have been investigated. Heteroatom doping (e.g., B, C, N, S, and F) has proven to be an effective strategy to extend the photoresponse from the UV to visible light region [16–20]. Moreover, theoretical calculations have also been performed, which suggest that anion doping of TiO_2 has a considerable effect on altering the band gap. The success of nitrogen doping in increasing the photocatalytic activity of TiO_2 in the visible light region provides a good opportunity for extensive applications such as the photocatalytic decomposition of dyes. Improvements in photocatalytic efficiency are usually attributed to a reduction in the band gap, due to either mixing of the N2p states with O2p states at the top of the valence band or the creation of a N-induced midgap level, as well as some impurities (e.g., NO_x and NH_x) [20–24]. Furthermore, it is known that the surface morphology of three dimensional nano heterostructures also has strong effects on the photocatalytic properties. Many reports have indicated that three dimensional hierarchical nano-heterostructures could not only promote the separation of electron hole pairs, but also provide high surface area for photocatalytic reactions and strong light scattering for enhancing light absorption, all of which are much favorable for photocatalytic process. To date, many experimental approaches have been developed to produce N-doped TiO_2 with visible light sensitivity, including sputtering, thermal nitridation, direct amination, and

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pulsed laser deposition. However, the synthesis of N-doped TiO_2 *via* a facile hydrothermal method has scarcely been reported. So far, nitrogen-doped TiO_2 are typically obtained by sintering the physical mixtures of the nitrogen-doped precursors (such as melamine, urea, cyanamide, and dicyandiamide), which usually results the aggregation of nitrogen contents on TiO_2 nanomaterials. The aggregation would reduce their specific surface area and hinder the interfacial charge transfer process of TiO_2 nano-heterostructures. How to avoid the aggregation of nitrogen contents in these nitrogen-doped TiO_2 nanoheterostructures? We note that the polymerization process in the above occurs on and out of the surface of TiO_2 nanomaterials simultaneously due to the relatively poor mass transfer rate and the non-uniform distribution of the solid precursor reactants. If the precursor of nitrogen precursors is urea, these precursor molecules could be preferentially and uniformly adsorbed on the surface of TiO_2 by molecular interactions. Therefore, the fast diffusion rate and good interface contacts in the reaction may favor the formation of uniform heterostructure with good controllability. Hydrothermal reactions are a promising strategy for fabricating composites due to their low cost, good product dispersion, and ease of operation for N doping at relatively low temperatures [25–27].

Graphene, a two-dimensional honeycomb-like network of carbonaceous material, has attracted much attention in photocatalytic applications for various reasons. Because of its high electron mobility and extended π−conjugation structures, graphene is considered to be an ideal electron acceptor and mediator for facilitating charge carrier separation. Graphene is also an emerging photosensitizer in TiO_2-based binary hybrids and it increases visible light absorption intensity for more efficient utilization of solar energy. Furthermore, the large surface area of graphene provides many surface active sites for catalytic reactions [28–31].

In this study, nitrogen-doped TiO_2 coatings on reduced graphene oxide (rGO), denoted as GN-TiO_2, were prepared by sol-gel and hydrothermal processes. Their photocatalytic efficiency was investigated through the photodegradation of an organic dye under visible light irradiation. The synergistic effect of the composites on photodegradation is discussed in detail.

2. Experimental

2.1. Synthesis of nitrogen-doped TiO_2 coatings on reduced graphene oxide

Firstly, graphene oxide (GO) was synthesized from natural flake graphite according to the improved synthesis [32]. Nitrogen-doped TiO_2 coatings on reduced graphene oxide were synthesized by a sonochemical synthesis and hydrothermal process. Firstly, the as-synthesized GO (0.2 g) was dispersed in 20 mL of ethanol (≥99.9%, Sigma-Aldrich) and 10 mL of deionized water, in which 0.4 g of urea (99.0%, OCI) was then dissolved. After stirring for 30 min, a certain amount of titanium (IV) isopropoxide (TTIP, 97%, Sigma-Aldrich) was added with vigorous stirring at ambient temperature. The prepared mixture was ultrasonicated in an ice bath for 30 min, then sealed in a Teflon-lined autoclave and kept at 180 °C for 6 h. After hydrothermal reaction, the solid products were collected and washed with ethanol, followed by drying at 80 °C. The obtained products were calcined at 400 °C for 2 h under H_2/Ar h to achieve complete reduction. The resultant powders were referred to as GN(x)-TiO_2, where x indicates the volume (mL) of TTIP added.

2.2. Characterization

Sample morphologies and surface images were obtained using high resolution scanning electron microscopy (HR-SEM, SU 8010, Hitachi), while crystal structures were investigated by X-ray diffraction analysis (XRD, D2 PHASER, Bruker). X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo scientific) analysis was performed with a 200 kV accelerating voltage and a monochromated Al Kα X-ray source. N_2 adsorption−desorption isotherms were measured to examine the specific surface area and pore structure using a gas adsorption analyzer (BELSORP, BEL). Before the analysis was conducted, the samples were degassed at 393 K for 24 h in order to obtain a residual pressure of $<10^{-6}$ mmHg.

2.3. Photocatalytic experiments

The photocatalytic activities of nitrogen-doped TiO_2 coatings on reduced graphene oxide were evaluated by observing the degradation of rhodamine B (RhB, >95%, Sigma-Aldrich) as the pollutant in a sealed quartz reaction vessel. The reaction vessel was filled with each prepared sample (10 mg) and RhB aqueous solution (10 ppm, 50 mL). A solar simulator (Sun 2000, ABET technology) was used as the light source to trigger photocatalytic degradation. In RhB degradation, aqueous samples were collected at regular intervals and RhB concentration was analyzed using a UV−Vis spectrophotometer (S-3100, Scinco) to record absorption bands at 555 nm. Each set of experiments was monitored for 2 h.

3. Results and discussion

3.1. Characterization

HR-SEM was used to observe the morphologies of as-synthesized pristine TiO_2, rGO, and GN3-TiO_2. Fig. 1a shows a typical HR-SEM image of TiO_2 particles prepared using the sol-gel process. The particle structure consists of approximately uniform round-shaped grains with a regular morphology and an average particle size of about 15–20 nm. As shown in Fig. 1b, the sheet-like structure of rGO was observed. Fig. 1c confirms the formation of entangled one-dimensional nanostructures, indicating a drop in particle diameter. During the hydrothermal process with GO and urea, the majority of TiO_2 particles kept their original morphology, with a little agglomeration observed, perhaps due to TiO_2 particles being wrapped up in rGO sheets. It is clear that the hydrothermal self-assembly reaction results in uniform composite materials of micron-sized rGO sheets and TiO_2 particles [33,34].

The XRD patterns for GO and rGO are shown in Fig. 2a, and the corresponding lattice constant, *d*, was calculated by Bragg's law [35]. A typical broad peak near $2\theta = 10.8°$, corresponding to a layer-to-layer distance (*d*-spacing) of ~0.811 nm, was observed for GO. A dramatic shift to higher 2θ angles (~26.1°), with a smaller *d*-spacing of ~0.439 nm, was observed for rGO. This reduction in *d*-spacing clearly indicated better ordering of the two-dimensional structure [36,37]. The results of XPS analysis are shown in Fig. 2b. The C1s core levels were compared in GO sheets obtained before and after reduction. The GO spectrum was deconvoluted into four peaks corresponding to the following functional groups: C═C/C−C (285.1 eV), C−O (hydroxyl and epoxy, 286.4 eV), C═O (carbonyl, 287.1 eV), O−C═O (carboxyl, 285.1 eV). The C1s core level of rGO showed that most oxygen-containing functional groups were significantly reduced during GO reduction using either of the two reduction procedures [38].

As shown in Fig. 3a, the diffraction peaks in the XRD pattern of pristine TiO_2 at $2\theta = 25, 37, 48, 53, 55, 63, 69,$ and $76°$ corresponded to (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (2 2 0), and (2 1 5) crystal planes, respectively, indicating the presence of an anatase structure (JCPDS card 21-1272) [39]. No significant change was observed in the XRD patterns of N−TiO_2 and GN3-TiO_2. These results demonstrated that the anatase phase of the prepared samples