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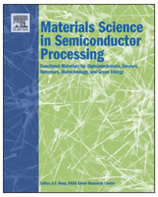

Enhanced photocatalytic activity of graphene oxide/titania nanosheets composites for methylene blue degradation

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ABSTRACT

In the present work, we report enhanced photocatalytic degradation of methylene blue dye in aqueous solution by using ultra-thin anatase TiO_2 nanosheets (NSs) combined with graphene oxide (GO) as a photocatalyst. The two-dimensional ultra-thin anatase TiO_2 NSs are fabricated via chemical exfoliation. By completely delaminating a lepidocrocite-type layered protonic titanate $H_xTi_{2-x/4}\square_{x/4}O_4 \cdot H_2O$ ($x=0.7$, □: vacancy) into individual layers through ion exchange with tetrabutylammonium (TBA^+) cations, well-dispersed ultra-thin colloidal $Ti_{0.91}O_2$ NSs with a lateral size up to a few micrometers are obtained. Subsequent acid treatment induces colloidal $Ti_{0.91}O_2$ to reassemble and precipitate into a gelation form, followed by thermal annealing to convert the $Ti_{0.91}O_2$ gelation into anatase TiO_2 nanosheets as photocatalyst for methylene blue degradation. TiO_2 NSs show a high photocatalytic degradation efficiency of 53.2% due to the ultra-thin thickness for facile electron transfering and large surface area for methylene blue absorption. Moreover, photocatalytic effect can be further improved by simply adding GO suspension to achieve colloidal self-assembly of GO and TiO_2 NSs. An optimal GO content of 3 wt% further increases the photocatalytic degradation efficiency to 91.2% due to faster electron–hole seperation and improved surface area provided by GO. This work provides a simple but effective approach by combing graphene oxide with TiO_2 nanosheets synthesized via the exfoliation method for methylene blue degradation.

1. Introduction

Research on semiconductor photocatalysis has attracted much interest due to an increasing demand of environmental remediation. Semiconducting titanium dioxide (TiO_2) has attracted considerable attention in the field of photocatalysis due to its chemical stability, non-toxicity, and readily available raw materials. It also finds wide applications in the fields of renewable energy, electrochemical energy and environmental protection such as dye-sensitized solar cells (DSSCs) [1–5], gas sensing [6–8], water splitting [9,10], biomedical materials [11,12], and lithium-ion batteries [13]. However, there are two major factors limiting application of TiO_2 in photocatalysis: (i) recombination of most of photogenerated electron–hole due to low mobility of charge carriers when migrating to the catalyst surface (e–h) pairs, and (ii) relatively large band gap which determines the energy necessary to create e–h pairs in the semiconductor for promoting photocatalytic processes.

Nanostructured TiO_2 photocatalyst with tailored features shows a higher photocatalyisis efficiency due to its effect on reducing e–h recombination rate [14–16]. Two-dimensional (2D) TiO_2 nanosheet (NS) is particularly interesting owing to several advantages described as follows. First, TiO_2 NS can

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serve as a hosting material to load guest functional nanomaterials and the resulting nanocomposite structure has advantages of both components in addition to other unique new properties. Second, 2D TiO_2 NSs and its derived nanocomposite materials can transform from 2D to 1D structure by scrolling into nanorolls or nanotubes [17]. Third, TiO_2 NS, especially ultra-thin TiO_2 NS, provides large interaction area between TiO_2 catalysts and organic pollutants. Since photocatalytic reactions mainly occur on the surface of photocatalyst, thus TiO_2 NS with large surface area will show higher degradation efficiency. Therefore, TiO_2 NSs demonstrate as a very promising catalyst for photocatalytic reactions. TiO_2 NSs can usually be synthesized via hydrothermal method using titanium salts as the precursor and hydrofluoric acid as the solvent [18,19]. However, hydrofluoric acid used in this hydrothermal method is corrosive and needs to be handled with extreme care. Another disadvantage is that the hydrothermal method relying on sealed autoclaves limits its application in large scale production of TiO_2 NSs.

It is critical to develop an effective and environmental friendly method to prepare TiO_2 NSs with high crystallinity and controllable dimensions. Quasi-titania nanosheets, with well-defined chemical composition of $Ti_{0.91}O_2$, can be synthesized by completely delaminating a lepidocrocite-type layered protonic titanate $H_xTi_{2-x/4}\square_{x/4}O_4\cdot H_2O$ ($x=0.7$, □: vacancy) into individual layers with tetrabutylammonium (TBA^+) ions using a soft-chemical exfoliation method [20,21]. The 2D colloidal exfoliated $Ti_{0.91}O_2$ NS has a unique structure with an extremely low thickness of 1 nm and a lateral size of micrometers. With such extremely high 2D anisotropy, $Ti_{0.91}O_2$ NS exhibits distinctive physical and chemical properties [22,23]. With these advantages, $Ti_{0.91}O_2$ NSs are expected to be a promising candidate for synthesizing TiO_2 NSs as catalyst used in photocatalytic reactions.

Many approaches have been applied to improve photocatalytic efficiency of TiO_2 by improving its charge separation efficiency, which is the main factor that restricts TiO_2 application. Graphene has recently drawn considerable interest for applications in photovoltaic devices owning to its very light weight, large surface area, and extremely high electron mobility ($\sim 15{,}000\ cm^2\ V^{-1}\ s^{-1}$) at room temperature [24–26]. It has been demonstrated that incorporation of graphene into TiO_2 NSs greatly facilitates electron transport. However, aggregation and self-assembly of graphene nanosheets in aqueous solution dramatically reduce their specific surface area/active sites owing to their hydrophobicity [27–29]. Graphene oxide (GO), a derivative of graphene, possesses a large number of oxygen functional groups on the nanosheet surface and shares similar advantages with graphene [31–33]. Moreover, light absorption of GO is much smaller than graphene, which favors light irradiation on the surface of TiO_2 [30,31]. As such, GO nanosheets can be an ideal electron acceptor for TiO_2 and can help to enhance e–h separation efficiency. Chen et al. prepared graphene oxide/TiO_2 composites using a modified sol–gel method and evaluated visible light driven photocatalytic performance of graphene oxide/TiO_2 composites for degradation of methyl orange [34]. Sha et al. synthesized GO supported ultrathin TiO_2 NSs using a one-pot hydrothermal method [35]. In this approach, with 5 wt% GO introduced, photocatalytic property was improved due to the increased specific surface area from $4.22\ m^2\ g^{-1}$ to $36.63\ m^2\ g^{-1}$ and accelerated separation of e–h pairs. However, these methods either involve complicated experimental set up or suffer from poor interfacial contact with GO surface due to TiO_2 agglomeration. Therefore, it is necessary to explore a simple and effective approach to solve these issues.

In the present work, ultra-thin TiO_2 NSs are synthesized using a soft-chemical exfoliation method. Photocatalytic activities of the ultra-thin TiO_2 NSs are evaluated via degradation of methylene blue ($C_{16}H_{18}N_3$–SCl, MB) dye under UV light irradiation. Moreover, the effect of GO on photocatalytic property of ultra-thin TiO_2 NSs is explored by simply adding GO aqueous solution to achieve colloidal self-assembly of GO and TiO_2 NSs. The as-prepared GO/TiO_2 NSs demonstrate improved photocatalytic activity due to enhanced charge separation efficiency and large specific surface area. In addition, GO content can be optimized to maximize photocatalytic activity of GO/TiO_2 NSs.

2. Experimental

Lamellar solids of lepidocrocite-type cesium titanate $Cs_xTi_{2-x/4}\square_{x/4}O_4$ (□: vacancy, $x=0.7$) were synthesized using a conventional solid-state calcination method [36,37]. A stoichiometric mixture of Cs_2CO_3 (Alfa Aser, 99.99%) and TiO_2 (anatase, 99%, Sigma-Aldrich) was calcinated with a molar ratio of 1:5.3 at 1073 K for 20 h. After cooling, the products were ground and calcinated repeatedly. Subsequent acid leaching converted them into a protonated form of $H_xTi_{2-x/4}\square_{x/4}O_4\cdot H_2O$ [20,21]. Protonated titanate was derived through repeated ion exchange of Cs with proton. The resulted powder (~2 g) was stirred in a 200 ml hydrochloric acid solution with a concentration of $1\ mol\ l^{-1}$ for 24 h. After Cs extraction was completed via four cycles of ion exchange, the acid-treated product was thoroughly washed with water to remove acid residue and dried under ambient condition.

The as-prepared $H_xTi_{2-x/4}\square_{x/4}O_4\cdot H_2O$ was treated with tetrabutylammonium hydroxide (TBAOH, $(C_4H_9)_4NOH$, ~40% solution, Fluka) to delaminate into $Ti_{0.91}O_2$ NSs. A weighed amount (2 g) of $H_xTi_{2-x/4}\square_{x/4}O_4\cdot H_2O$ was shaken vigorously in an aqueous solution (500 ml) of TBA hydroxide at room temperature for two weeks. The amount of TBA hydroxide was 5-fold excess to the exchangeable capacity of $H_xTi_{2-x/4}\square_{x/4}O_4\cdot H_2O$ ($4.12\ meq\ g^{-1}$). Typically, 100 ml colloidal suspension of $Ti_{0.91}O_2$ NSs was poured into 100 ml of HCl solution ($1\ mol\ l^{-1}$). Wool-like precipitates were yielded and the mixture was stirred overnight. After filtration and washing with distilled water, a post-calcination process was necessary for removing organic residues and forming a high-crystalline phase. The obtained solids were then heated at 450 °C in air for 3 h to produce anatase TiO_2 NSs. Single-layer graphene oxide (GO) (ACS Material, LLC) was dispersed in DI water, and then sonicated for 1 h to produce a uniform suspension. The GO/TiO_2 nanosheets are fabricated by mixing various amounts of GO suspension with 5 mg TiO_2 NSs; the weight