Highly active TiO$_2$/g-C$_3$N$_4$/G photocatalyst with extended spectral response towards selective reduction of nitrobenzene

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ABSTRACT

A simple self-assembly photochemical reduction method has been proposed to prepare highly photocatalytic TiO$_2$ nanowire/g-C$_3$N$_4$ nanosheet/graphene heterostructures (TiO$_2$/g-C$_3$N$_4$/G). In this hybrid structure, graphene enhances the charge transportation during photocatalytic process, and TiO$_2$ nanowires prevent graphene and g-C$_3$N$_4$ from restacking. Meanwhile, g-C$_3$N$_4$ with a more suitable band gap, extends the adsorption edge of the TiO$_2$/g-C$_3$N$_4$/G composite to visual-region. Benefiting from the positive synergetic effect, 97% of nitrobenzene can be selectively reduced within 4 h by using TiO$_2$/g-C$_3$N$_4$/G as the photocatalyst. The TiO$_2$/g-C$_3$N$_4$/G composite with 3D structure demonstrates a great potential in selective oxidation and reduction of organics for the synthesis of high added-value organic compounds.

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1. Introduction

Semiconductor based photocatalysis, a promising green chemical technique, is an approach to utilizing solar energy for hydrogen production [1], degradation of pollutions [2] and selective organic synthesis [3]. It is worth noting that the selective oxidation and reduction of organics for the synthesis of high added-value organic compounds have attracted much attention in recent years [4–6]. Aniline is one of the most important organic compounds and intermediates in the production of pharmaceuticals, food additives, agrochemicals, dye, and etc. [7,8]. In the past years, catalytic hydrogenation is a widely used for reducing nitrobenzene to aniline, which usually apply Pt, Pd, Au and transition metal as catalysts, NaBH$_4$ or H$_2$ reducing agents as additives. Additionally, this conversion process usually requires harsh reaction conditions, which greatly increases the product cost and fabrication difficult [8–11].

Recently, it is found that photocatalytic reduction technology demonstrates a great promising in the study of selective organic synthesis. Being without involving of any environmentally unfriendly reducing agents and harsh reaction conditions, photocatalytic reduction is able to synthesize aniline in a green, low cost and effective way. As we known, titanium dioxide (TiO$_2$) is a widely studied photocatalyst material possesses many advantages including high resistance to photocorrosion, chemical inertness, nontoxicity and low cost. However, the single TiO$_2$ semiconductor catalyst usually owns a poor activity, narrow spectral response and limited efficient electron transportation, which greatly degrades its performance. Recently, the fabrication of TiO$_2$ based composite materials is proved to be an effective strategy to improve its chemical activities [12–15]. In order to improve the poor charge transport property originated from TiO$_2$, Zhang et al. incorporated TiO$_2$ with graphene for the first time in 2010 [16]. The results demonstrated that the trapping capability of graphene enhanced electron transportation and the as fabricated composite exhibited a high photocatalytic activity. Meanwhile, the easier organic molecule adsorption derived from the extended sp^2 hybrid carbon framework in graphene, along with its high UV light transparency, also contributed to the improvement of the photocatalytic activity [17–19]. Unfortunately, as TiO$_2$ nanoparticles own a large surface energy, they tend to aggregate during the reaction. Additionally, those TiO$_2$ in the form of nanoparticles cannot against the strong

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Van del Walls force between each graphene layer, which made them incapable of preventing graphene from restacking. In this context, efforts have been made to tailoring the morphology of TiO_2, with a hope of resolving the aforementioned restacking and aggregation issues. Recently, one-dimensional TiO_2 nanostructures, including nanowires (NWs) [20,21], nanobelts [22–24] and so on, have triggered an explosion of research interests. For instance, Pan et al. [25] compared photocatalytic degradation performance between graphene/TiO_2 NWs and graphene/TiO_2 NPs composites and demonstrated that TiO_2 NWs, in comparison with TiO_2 NPs, had more uniform dispersion on graphene with less agglomeration. Also, the intercrossed TiO_2 NWs acted as the spacer between graphene nanosheets, which effectively prevented graphene from restacking, thereby endowing the composite catalyst with high stability and photocatalytic activity. More interestingly, as demonstrated by Sang et al. [22], in TiO_2 nanobelt/G composite, TiO_2 nanobelt with the unique 1D nanostructure can promote fast and efficient electron transport along the axial direction, which was conducive to the carrier separation during the photocatalytic process. It is therefore anticipated that the incorporation of graphene and 1D nanostructured TiO_2 would achieve dramatically enhanced charge transport properties associated with no obvious graphene restacking and TiO_2 agglomeration [26,27]. However, being limited by the narrow spectrum response stemmed from large band gap of TiO_2, the performance of these 1D TiO_2/graphene composite is still far from satisfactory.

In order to enhance the utilization of sunlight, namely extending the adsorption edge to visible light region, an effective strategy that incorporates TiO_2 based composite with other visible-light catalysts has been proposed. Visible-light catalysts previously investigated includes CdS [28], $BiVO_4$ [29], g-C_3N_4 [30,31] etc. Among them, graphitic carbon nitride (g-C_3N_4), with a unique graphene-like 2D structure together with a band gap of about 2.7 eV, has attracted enormous attention as a photocatalyst. Similar to graphene, g-C_3N_4 suffers from the inevitable restacking when being used alone. More seriously, it also possesses high recombination rate of photo-generated electron-hole pairs, which poses detrimental effect on its performance in photocatalysis. Thus, various strategies have been applied to overcome these shortcomings. For instance, Yang's group reported the synthesis of free-standing g-C_3N_4 nanosheets by liquid phase exfoliation in isopropanol [32]. The ultrathin g-C_3N_4 nanosheets, with large aspect ratios, high surface area and stoichiometric N/C ratio, exhibited good photocatalytic activity towards hydrogen evolution owing to the enhanced visible light absorption and improved photoluminescence quantum yield. Moreover, heterojunctions formed between different semiconductor materials, such as g-C_3N_4/Graphene [33], g-C_3N_4/CdS/G [34], Ag@$AgVO_3$/G/PCN [35], can create great potential as the driving force to improve the separation of electron-hole pairs, which are proven to be effective photocatalysts to degrade organic pollutants under illumination.

Inspired by aforementioned insights, the TiO_2 NWs/g-C_3N_4/G nanocomposites were elaborately fabricated in this study. Specifically, graphene was introduced to enhance the charge transportation and separation during photocatalytic process. The incorporation of TiO_2 NWs were anticipated to show less agglomeration compared to that in nanoparticle form. Besides, they can act as skeleton between 2D nanosheet, thus preventing graphene and g-C_3N_4 from restacking. More importantly, g-C_3N_4 with a more suitable band gap extended the adsorption edge of the TiO_2 NWs/g-C_3N_4/G composite to visual-region, which significantly improved its photocatalytic performance towards selective reduction of nitrobenzene to aniline. It is found that the as fabricated TiO_2/g-C_3N_4/G composites show significantly improved photocatalytic performance with a conversion of over 97% during a reaction

lasting for 4 h, exhibiting great potential in the field of selective photo reduction of organics.

2. Experimental

2.1. Synthesis of TiO_2 nanowires

TiO_2 NWs were synthesized by a hydrothermal method. Commercially available Degussa P25 was dissolved in 10 M NaOH solution and the concentration of P25 was 7.5 mg/mL. The homogeneous suspension was obtained by sonicating for 10 min and magnetically stirring for 30 min. Then the mixture was transferred to a Teflon vessel held in a stainless steel vessel at 180 °C for 12 h $Na_2Ti_8O_{17}$ nanowire hydrogels were obtained and then ion exchanged into $H_2Ti_8O_{17}$ by acid treatment (0.2 M HNO_3). After that, the hydrogen titanate nanowire materials were washed with excess deionized water until the filtrate became neutral and freeze-dried for further use. Finally, $H_2Ti_8O_{17}$ NWs were transformed into TiO_2 NWs by calcination at 600 °C for 4 h.

2.2. Synthesis of TiO_2/g-C_3N_4/G nanocomposites

GO was prepared from natural graphite powder (Alfa Aesar, 325 mesh) by a modified Hummer's method [36]. Bulk g-C_3N_4 was prepared by heating melamine from room temperature to 600 °C with a ramp rate of 2 °C/min and kept at this temperature for 4 h [1]. g-C_3N_4 nanosheets were fabricated by one-pot exfoliation of bulk g-C_3N_4 powder in isopropanol as solvent via a sonication. TiO_2/g-C_3N_4/G heterojunctions were prepared via photochemical reduction self-assembly methods. Briefly, 20 mg GO was dispersed in 30 mL ethanol by ultrasonic to obtain Solution A. 150 mg g-C_3N_4 nanosheets was dispersed in 50 mL ethanol by ultrasonic to make Solution B. 50 mg TiO_2 nanowires were dispersed in 30 mL ethanol under soft ultrasonication to obtain Solution C. Solutions A, B and C were mixed and stirred for 60 min. Then, the mixture was irradiated under 300 W xenon lamp for 4 h with stirring. The solution changed its color from brown to black, indicating that GO was reduced by the photocatalysts of g-C_3N_4 and TiO_2 NWs and ethanol was the vacancy sacrificial reagent. The TiO_2/g-C_3N_4/G heteroconjugates were obtained by washing with deionized water. The TiO_2/g-C_3N_4/G powder was collected by vacuum drying for further experiments. For comparison, TiO_2/G, g-C_3N_4/G were also prepared using similar methods without the presence of g-C_3N_4 and TiO_2, respectively.

2.3. Material characterization

The powder X-ray diffraction (XRD) measurements of as-prepared samples were recorded on the Bruker D8 Advance Germany using a graphite monochromator with Cu-Kα radiation (λ = 1.5406 Å). Raman spectra were recorded at room temperature using (InVia Reflex, Renishaw, UK) with a 532 nm laser excitation in the range of 800–3500 cm^{-1}. X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-Alpha American with an Al Kα X-ray source) was used to measure the elemental composition of samples. The specific surface area was measured by using a nitrogen gas sorption surface area tester (JW-BK222, Beijing JWGB) and calculated by the Brunauer-Emmett-Teller (BET) method. The morphology of samples was characterized by FEI Quanta 200F scanning electron microscope (SEM) and the transmission electron microscope (TEM, Tecnai G2 F20) equipped with selected area electron diffraction (SAED). A drop of the g-C_3N_4 supernatant was deposited on a mica substrate for atomic force microscope (AFM) observation (Bruker, Multimode 8). Thermal gravimetric analysis (TGA) was conducted in oxygen at a heating rate of 10 °C/min. The diffuse reflectance absorption spectra (DRS) of the samples were recorded