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Graphene oxide embedded into TiO_2 nanofiber: Effective hybrid photocatalyst for solar conversion

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ABSTRACT

One-dimensional TiO_2 nanofibers (NFs) in which graphene oxide (GO) sheets were incorporated (GO–TiO_2 NFs) were prepared by using a sol–gel method and an electro-spinning technique. Unlike typical graphene/TiO_2 composites that have TiO_2 nanoparticles loaded on graphene/GO sheets, GO in GO–TiO_2 NF is embedded within the matrix of TiO_2 NF that consists of closely packed TiO_2 nanoparticles. GO–TiO_2 NF was characterized by various analytical methods and tested for its photocatalytic and photoelectrochemical activities. The inclusion of GO sheets in TiO_2 NF improved the photocatalytic and photoelectrochemical activities: the photocatalytic hydrogen production and photocurrent generation increased by 1.7 and 8.5 times, respectively. GO sheets embedded in TiO_2 NFs can improve the interparticle connection and facilitate the charge pair separation by serving as an *in-built* electron collector and conduit. Therefore, the enhanced photo(electro)chemical activities in the presence of embedded GOs are related to the retarded charge recombination rate and the lower charge transfer resistance. The advantages of GO–TiO_2 NF were confirmed by comparing with a different composite of GO/TiO_2 NF having GO sheets bound to the external surface of TiO_2 NF (GO(s)–TiO_2 NF). The photocatalytic hydrogen production with GO–TiO_2 NF was higher than GO(s)–TiO_2 NF both in the absence and presence of Pt cocatalyst, which is mainly ascribed to the stronger electronic coupling between GO sheets and TiO_2 matrix and the reduced light shielding by GO buried inside of TiO_2 NF. Whether GO sheets are present within the NF matrix or on the external surface of NF critically influences the photocatalytic activity.

1. Introduction

TiO_2 is one of the most popular and successful photocatalysts employed in many application fields because it is abundant, is stable in acidic and alkaline aqueous solution, and has strong photo-oxidation power [1–4]. However, some critical drawbacks of TiO_2 limit its practical performance. The large bandgap of TiO_2 ($\sim$3 eV) restricts the active working range below $\lambda < 400$ nm, and therefore, TiO_2 can be activated by UV light only which accounts for less than 5% of the total solar energy [5]. The poor electron–hole separation efficiency is another critical drawback that is responsible for the low photocatalytic activity [6]. To overcome these problems, various strategies have been employed such as doping with metallic or non-metallic elements [7,8], hybridization with carbon materials [9–12], and making unique geometry [13–15]. In particular, semiconductors with one-dimensional (1-D) structures such as nanowires, nanotubes, and nanorods have attracted much interest because of their unique properties compared to bulk materials. 1-D structures of TiO_2 have been applied to water-splitting, environmental remediation, self-cleaning, and electrical devices [16–18]. The most outstanding property of 1-D structural TiO_2 is that the short diffusion length to the surface region enhances the charge separation efficiency with reducing the chance of carrier recombination [19,20]. Such property should enhance the photocatalytic reactions occurring on 1-D structural TiO_2. For example, in photocatalytic and photoelectrochemical water-splitting that requires the multi-electron transfer, the efficient charge separation on 1-D structures is extremely important [21,22].

The low photocatalytic efficiency of TiO_2 can be often enhanced by the hybridization with other components such as carbon nanomaterials [23,24]. Especially, the hybridization with graphene has received wide attention as an effective method to increase the adsorption of substrates and the charge separation efficiency [25–28]. When graphene is combined with TiO_2, the photogenerated electrons in TiO_2 can easily transfer from the conduction band to graphene because the two dimensional π-conjugated structure of graphene sheet serves as a good reservoir of electrons. As a result, the composite of TiO_2/graphene effectively suppresses the charge carrier recombination [29,30]. However, in spite of unique

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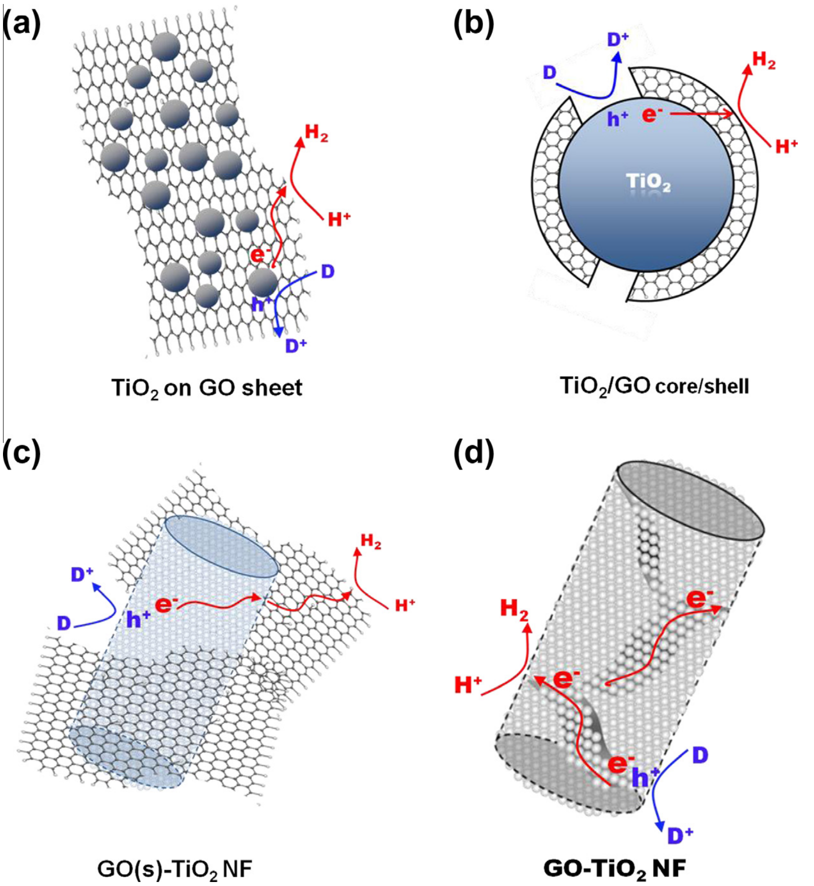
properties of graphene–TiO_2 hybrids, the photocatalytic efficiency was not superior to bare TiO_2 in some studies [11,31]. One of the most critical parameters that affect the photocatalytic properties of TiO_2/graphene composite is the interfacial contact between the graphene sheet and TiO_2 nanoparticles. Most TiO_2/graphene composites employed μm-sized sheets of graphene on which TiO_2 nanoparticles were loaded, but this geometry suffers from the low contact area between graphene and TiO_2. The binding force between TiO_2 and graphene being mostly electrostatic with this structural geometry, and most TiO_2 nanoparticles are detached from graphene sheets at pH higher than the point of zero charge (PZC) of TiO_2 ($pH_{pzc} \approx 6$) [32]. To enhance the interfacial contact area, we recently introduced a self-assembled core/shell structure that consists of TiO_2 nanoparticles (core) coated with thin layers of graphene (shell) to demonstrate high photocatalytic and photoelectrochemical activity [11]. However, the graphene layers surrounding TiO_2 particles at higher graphene loading can interfere with the light absorption by TiO_2 and block the active surface sites, which may reduce photocatalytic efficiency [11,33,34].

Here, we report a new hybrid geometry that has graphene oxide (GO) sheets embedded into the matrix of TiO_2 nanofiber (NF) for higher photocatalytic and photoelectrochemical activity. Scheme 1 compares the various structures of the composite consisting of TiO_2 and graphene sheets: (a and b) structures were previously studied as mentioned above and (c and d) structures studied in this work. TiO_2 NF which consists of densely packed TiO_2 nanoparticles facilitates the interparticle charge transfer/separation within the NF matrix [35]. The incorporation of GO sheets into the matrix of TiO_2 NF improves the interparticle connection among densely packed TiO_2 nanoparticles and further facilitates the electron–hole pair separation by serving as an *inbuilt* electron collector and conduit. The characterization and the enhanced photo(electro)catalytic behaviors of the GO-incorporated TiO_2 NF structure are investigated and discussed to test the role of this new geometry as an efficient solar photocatalytic material.

2. Experimental

2.1. Preparation of graphene oxide (GO)

Graphene oxide was prepared by following the modified Hummers method [36]. Three gram of graphite (SP-1 grade 200 mesh, Bay carbon Inc.) was added into a mixture of concentrated H_2SO_4 (150 mL) and $NaNO_3$ (1.5 g) with vigorous stirring. After 1 h, 9 g of $KMnO_4$ was added slowly into the mixture solution and the temperature increased to 35 °C under stirring for 7 h. Additional 9 g of $KMnO_4$ was added, and the stirring continued for 12 h at the constant temperature of 35 °C. The obtained mixture was cooled down to room temperature and poured into 500 mL of H_2O_2 solution (490 mL of water + 10 mL of 30 wt% H_2O_2) in an ice bath. The diluted mixture was filtered and washed 3 times with 200 mL of 1 M HCl. The obtained solid product was redispersed in water and dialyzed for 2 weeks with dialysis membrane (Spectra/Por, MWCO: 6–8000) to remove remaining acids and reactants. The dialyzed mixture was centrifuged (12,000 rpm for 1 h), and the supernatant was removed. The obtained graphite oxide was redispersed in water or DMF and was ultrasonicated (JAC 4020, 400 W, Sonic) for 30–120 min in order to obtain exfoliated graphene oxide.



Scheme 1. Illustration of the various composite structures of TiO_2 and graphene sheets and the associated charge transfers for hydrogen production: (a) TiO_2 nanoparticles loaded on graphene sheet, (b) graphene layers covering TiO_2 nanoparticles, (c) graphene sheets coupled with the external surface of TiO_2 nanofibers, and (d) graphene sheets embedded into the matrix of TiO_2 nanofibers.