



Self-assembled TiO₂ agglomerates hybridized with reduced-graphene oxide: A high-performance hybrid photocatalyst for solar energy conversion



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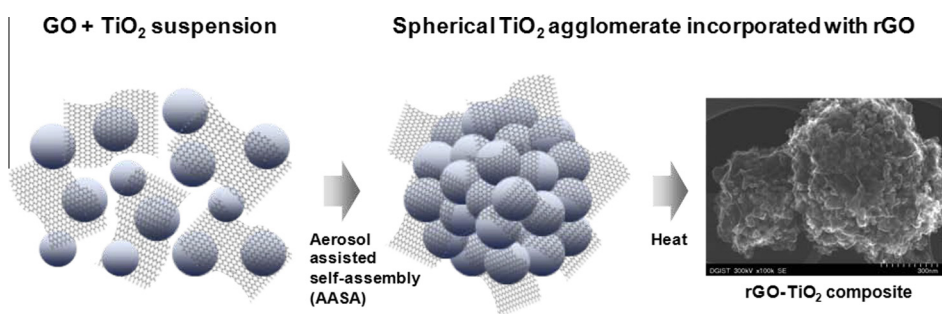
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HIGHLIGHTS

- We developed new hybrid geometry of TiO₂ and reduced-graphene oxides.
- The new geometry of the rGO–TiO₂ was prepared by the self-assembled agglomeration.
- The rGO–TiO₂ composite exhibited the enhanced photocatalytic activity.
- The new geometry would be responsible for minimized light-shielding effect of rGO.
- The rGO–TiO₂ composite can be considered as a promising hybrid photocatalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

Spherical TiO₂ agglomerates incorporated with reduced-graphene oxide (rGO) sheets were fabricated using aerosol assisted self-assembly. Compared to that of conventional graphene–TiO₂ composites, the new hybrid geometry of the self-assembled agglomeration of TiO₂ and rGO enabled a porous structure, a more efficient charge separation through interconnected TiO₂ nanoparticles and rGO, and improved the contact between TiO₂ and rGO to maximize the role of rGO as an electron reservoir. The as-prepared rGO–TiO₂ composites were characterized with a diverse range of analytical techniques, and their photocatalytic activity was tested in terms of H₂ production and gaseous CH₃CHO degradation. The incorporation of the rGO sheets into the TiO₂ agglomerates promoted the photocatalytic H₂ production and CH₃CHO oxidation; our results showed that the performance of our systems is directly proportional to the content of rGO (when added up to 10 wt%). This finding confirmed that rGO, acting as an electron collector and mediator, can facilitate charge-pair separation; only a small light-shielding effect by rGO was observed. Furthermore, open-circuit potential decay measurements revealed that the presence of rGO in the agglomerated TiO₂ can significantly suppress charge recombination; this further confirmed the role of rGO as an effective electron conduit. The new geometry of the rGO–TiO₂ composite proposed in this work shows several advantages compared to various types of graphene–TiO₂ composites previously reported,

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such as the stronger electronic coupling between rGO sheets and TiO₂, minimized light-shielding effect by rGO (even when a relatively large amount of rGO is used), and facile scale-up for mass production. Therefore, our rGO–TiO₂ composite can be considered as a promising hybrid photocatalyst for solar energy conversion.

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1. Introduction

Since its first observation by Novoselov et al. in 2004 [1], graphene has been attracting much attention in a variety of fields. Graphene, a sp²-hybridized two-dimensional carbon sheet with one-atom thickness, possesses many unique properties, such as high charge-carrier mobility [2], large theoretical specific surface area [3], excellent optical transparency [4], and mechanical flexibility [5]. Owing to a peculiar two-dimensional structure and a high electrical conductivity, graphene has been used as a co-catalyst in combination with semiconductors, as an electrical mediator for the improvement of the photo(electro)catalytic activity of semiconductors to convert solar energy, and for environmental applications [6–8].

TiO₂, one of the most popular photocatalysts, has been widely applied in hydrogen production, environmental pollutant degradation, self-cleaning, and electrical devices [9,10]. Albeit many advantages, such as its abundance, strong oxidation power, and high stability [11], the fast electron–hole recombination (ns–μs domain) of TiO₂ represents a serious drawback, which leads to a low photocatalytic activity [12,13]. The fast electron–hole recombination of TiO₂ can be drastically improved by hybridization with carbon nanomaterials [14]. Among these, graphene materials, including graphene oxide (GO) and reduced-graphene oxide (rGO), have received great attention because of their suitable electrical properties [15–19]. Once TiO₂ is hybridized with graphene under illumination, the photogenerated electrons in the conduction band (CB) of TiO₂ can easily transfer to graphene, which acts as a reservoir of electrons, owing to its Fermi-level that is positively lied to that of TiO₂ [20].

However, when TiO₂ nanoparticles (NPs) are combined with graphene sheets, their structural mismatch (nm-sized spherical shape of TiO₂ particles and μm-sized two-dimensional sheets of graphene) causes serious drawbacks. Since the loaded TiO₂ NPs are easily accumulated along the wrinkles of the graphene sheets, the contact area between the graphene sheets and the loaded TiO₂ NPs may be too small; this can in turn reduce the synergistic effect of their photocatalytic activity [15,21]. Several recent studies have attempted to enhance the photocatalytic activity of GO or rGO–TiO₂ hybrids by increasing the interfacial contact area; this was achieved by: (1) a self-assembled core/shell structure that consists of TiO₂ NPs (core) coated with thin layers of nano GO (shell) [21]; (2) controlling the surface of GO or TiO₂ NPs with the functionalization with specific groups [22,23]; (3) layered titanate and rGO hybrids characterized by a thin two-dimensional nanoplate structure, obtained by electrostatically derived self-assembly [24]; (4) distributing TiO₂ nanowires instead of TiO₂ NPs on rGO, which partly prevents agglomeration in high contact areas [15].

Here, we report a new hybrid geometry that consists of spherical TiO₂ agglomerates incorporated with rGO sheets, fabricated by aerosol assisted self-assembly (AASA) and subsequent heat treatment. Spherical GO–TiO₂ agglomerates with a uniformly controlled size were prepared by evaporating droplets formed from aqueous suspensions of TiO₂ NPs and GO, followed by heat treatment to thermally reduce GO to obtain rGO–TiO₂ composites and simultaneously achieve sintering of TiO₂ aggregates for rigid inter-particle network. The AASA method is of particular interest

due to its many advantages, e.g., it is simple, cost-effective, and is a facile process for scale-up [25,26]. Agglomeration of the rGO–TiO₂ composite renders the structure porous (which is a favorable feature for adsorption-initiated transformation reactions), facilitates charge transfer through interconnected TiO₂ NPs [27] and rGO sheets, and significantly improves the contact between TiO₂ NPs and rGO sheets compared to hybrid materials formed by electrostatic force only. These properties may lead to an enhanced photocatalytic performance of the as-prepared catalysts. To prove this point and to clarify the role of the proposed geometry as an efficient hybrid photocatalyst for solar energy conversion, the as-prepared rGO–TiO₂ system was characterized, and its photo(electro)catalytic behavior was systematically investigated.

2. Experimental

2.1. Preparation of the GO colloid

GO was prepared by the modified Hummers' method [28], which is based on the oxidation of graphite powder (Alfa Aesar, 99.9%) using H₂SO₄ (Junsei, 95%) and KMnO₄ (Junsei, 99.3%) with a pre-oxidation step. The mixture of the graphite powder with a strong oxidizing agent was filtered, washed, and dried. The obtained solid product was redispersed in distilled water via mechanical agitation; as previously described [29,30], sonication was performed using a table-top ultrasonic bath to produce a colloidal solution of exfoliated GO.

2.2. Preparation of the reduced GO–TiO₂ composites

The GO colloidal solution and TiO₂ particles (Degussa, P25) were dispersed into distilled water with different weight ratios (wt%) of GO/TiO₂, ranging from 0.01% to 10%, over a fixed TiO₂ concentration of 0.1 wt% in the colloidal mixture solution. The resulting mixture solution was used as an aerosol precursor for the preparation of porous rGO–TiO₂ composites. The experimental apparatus for AASA consisted of an ultrasonic atomizer, an electrical tubular furnace, and a filter sampler. The ultrasonic atomizer generates micron-sized droplets of the precursor solution. The droplets were carried into a furnace operated at 200 °C with a flow gas (argon, 1 L/min), resulting in the evaporation of water, and the self-assembly of GO and TiO₂. The fabricated GO–TiO₂ agglomerates were then collected by a heated Teflon membrane filter to prevent condensation. These were calcined at 800 °C for 10 min using a tubular furnace under argon atmosphere to complete the thermal reduction of GO and to simultaneously strengthen the interparticle connection of the rGO–TiO₂ composites. The prepared samples are hereinafter denoted as rGO-T-wt%, according to the wt% of rGO to TiO₂ NPs.

2.3. Characterization of the rGO–TiO₂ composites

Surface morphology images were obtained using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800, Japan). Transmission-electron micrographs were obtained with high-resolution transmission electron microscopy (HR-TEM, JEM-2200FS,

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