Recent advances in the synthesis and energy applications of TiO$_2$-graphene nanohybrids

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ABSTRACT

Owing to its excellent optical, electronic properties, good chemical and thermal stability, titanium dioxide (TiO$_2$) has been applied in promising energy technologies including new dye-sensitized solar cells, rechargeable batteries, supercapacitors, photocatalysts and gas sensors in recent years. However, wide band gap and poor electron transporting ability of TiO$_2$ has largely limited its application in some aspects like photocatalytic hydrogen generation and lithium ion batteries. Therefore, the modification of TiO$_2$ is essential for improving its optical and electrical properties. Graphene (GR), a two dimensional carbon nanostructure, is an ideal material to modify TiO$_2$ owing to its excellent electronic transport properties, exceptional thermal, and electrical conductivity. Compared to a pure TiO$_2$ nanostructure, the conjugation of GR leads to the increase of its adsorption capacity and photocatalytic activity, and improve the electrical conductivity and Li-ion diffusion pathways. In this review, we have firstly discussed pure TiO$_2$ nanostructures and introduced different methods for the preparation of TiO$_2$-graphene nanohybrids (TiO$_2$-GRNHs), and then discussed the practical applications of the TiO$_2$-GRNHs in different energy technologies. It is expected that the continuous breakthroughs in the synthesis and modifications of TiO$_2$-GRNHs will bring new high-performance materials with exotic properties and potential applications in emerging energy technologies.

1. Introduction

As a semi-conductor, titanium dioxide (TiO$_2$) has aroused great attention because of its excellent chemical and physical properties [1–6]. Compared with other materials, TiO$_2$ is probably the most suitable material for photocatalysis because it has the most efficient photo-activity, the lowest cost, the highest stability and the highest safety [7–14]. Owing to its high specific energy density and abundant availability, TiO$_2$ has also been promising for supercapacitors [15]. However, TiO$_2$ has a large band-gap [16–18], which largely limits the reaction of photocatalytic hydrogen. Therefore, many efforts have been made to synthesize doped TiO$_2$, such as M-TiO$_2$ (M = Ag [19–22], Pt [23], Fe [24]), sulfur-TiO$_2$ and carbon-TiO$_2$ nanocomposites [25–27] to solve these problems. Normally, these metal materials have poor thermal stability and exhibit a remarkably increased electron/hole recombination in defect sites, which results in a low photocatalytic efficiency [28]. In addition, one of disadvantages is that the use of expensive noble metals raises the material cost.

Compared to M-TiO$_2$ and sulfur-TiO$_2$ composites, carbon-doped

TiO$_2$ is a promising candidate because it is not only cheaper than the noble metal, but also shows good conductivity and strong absorption of light, which contributes to effective photo-degradation of pollutants [29,30]. In addition, TiO$_2$-carbon composites can also show good photocatalytic activity under UV light [31,32]. As one of the most popular two-dimensional (2D) graphitic carbon materials, graphene (GR) possesses excellent physical and chemical properties [33,34]. Therefore, compared to pure materials, GR-based composite materials exhibit enhanced activities due to the synergistic effect of GR component and TiO$_2$ [35,36]. Up to date, numerous research groups have been taking efforts to explore the fabrication and applications of TiO$_2$-GR nanohybrids (TiO$_2$-GRNHs) and the results are relatively satisfying. For example, Wang et al. prepared TiO$_2$-GRNHs via a facile hydrothermal reaction of graphene oxide (GO) and TiO$_2$ in an ethanol-water solvent [37]. The result showed that the TiO$_2$-GRNH was able to exhibit much higher photocatalytic degradation of methylene blue (residual quantity of 80% after 90 min) than that of the bare TiO$_2$ (residual quantity of 20% after 90 min). Besides, Qiu et al. synthesized TiO$_2$-reduced graphene oxide (TiO$_2$-rGO) nanohybrid and the TiO$_2$-rGO sample exhibited
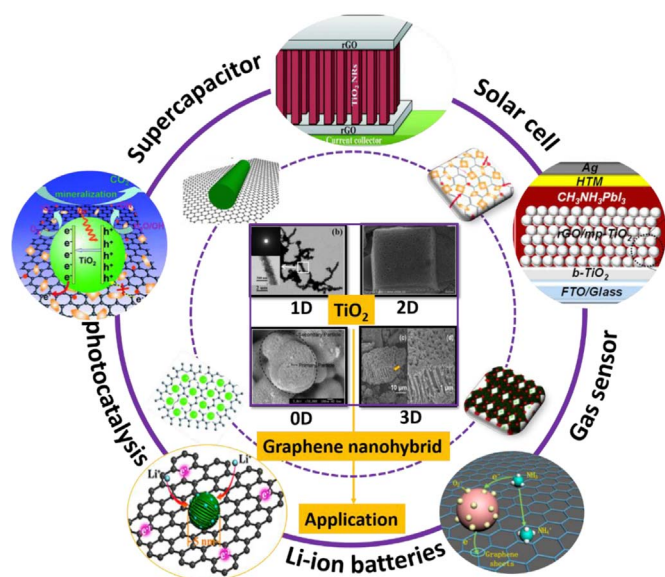
Fig. 1. Scheme of the applications of TiO_2-GRNH in different fields.

much higher specific capacity at the first discharge and charge (546 and 296 mA h g^{-1}) than the pure TiO_2 sample (395 and 160 mA h g^{-1}) [38].

In this review, we not only discussed the performance and nanostructure of pure TiO_2 but also explained the enhancing mechanism of GR for preparing TiO_2-GRNHs. In addition, we introduced the different methods for preparation of TiO_2-GRNHs such as hydrothermal method, solvent method, self-assembly, electrospinning and other methods. Besides, we also briefly illustrated the applications in TiO_2-GRNHs in Li-ion batteries, photocatalytic reaction, supercapacitor, solar cells and gas sensors (Fig. 1). At last, we made a conclusion and prospect of TiO_2-GRNHs, which would make continuous breakthroughs in the emerging energy technologies.

2. Performance and nanostructure of TiO_2

2.1. The performance of pure TiO_2

Since Fujishima and Honda firstly reported the phenomenon of photocatalytic splitting of water on a TiO_2 electrode in 1972 [39], studies about TiO_2 materials have become more and more attractive [40–42]. TiO_2, as one of semiconductors, exhibits excellent optical activity and electrical properties resulting from the band gap. Active oxides can be produced because of the interband transition of electrons under UV light illumination. Therefore, Most of organic dyes, some drugs like antibiotics that are not susceptible of degradation could also be easily degraded by employing TiO_2-based materials [14]. In addition, some studies confirmed that heat could improve the photocatalytic activity, suggesting the significance of an accurate temperature control in photocatalytic efficiency measurements [43].

In addition, TiO_2 is also an important material for constructing dye-sensitized solar cells (DSSCs) ascribing to its enormous contribution to anchoring of dye molecules, as well as the transfer and separation of charge carriers [44]. Compared with the conventional TiO_2 nanoparticles, the present ultra-fine TiO_2 nanotubes can not only reduce the electron recombination, but also supply a larger surface area for dye adsorption and display high conversion efficiency [45]. Fan et al. anatase TiO_2 nanosheets with exposed {001} facets have been applied to fabricate porous electrodes for DSSCs [45].

Especially, much attention has been paid to nanostructured TiO_2 for Li insertion, because it is not only a low-voltage insertion host for Li, but also a fast Li insertion/extraction host. These characteristics make it a potential anode material for high-power Li-ion batteries, avoiding the formation of a passivation layer at the contact to the liquid electrolyte. Importantly, one-dimensional (1D) mesoporous nanoarchitectures have gained more attention because they can guarantee high electrode-electrolyte contact area, shorten diffusion distances for Li^+ transport, and enable good accommodation of volume changes during cycling [46].

2.2. Different dimensional nanostructure of TiO_2

Recently, nanostructures including TiO_2 nanoparticles from 10 to 400 nm [45,47], 1D nanotubes and nanowires, 2D nanosheets with sizes approaching 100 nm and three-dimensional (3D) porous structured materials have been intensively investigated to confirm the differences of performance. It is found that the electrochemical performance of TiO_2 electrodes strongly depend on the morphology and the porosity of the structure [46].

2.2.1. 0D TiO_2 nanoparticles

Although 0D TiO_2 nanoparticles as basic structure have been studied for many years, the size, morphology, crystal form and photocatalytic activity are still worth researching in different synthesis methods. For example, Lee et al. reported a two-step sol-gel method to prepare TiO_2 nanoparticles with various shapes [48]. In this work, a stock solution of Ti^{4+} was firstly prepared, then the mixture aged in an autoclave after adjusting pH from 8.5 to 10.5. At the first aging step, a hydrolyzed gel network is formed under 100 °C for 24 h, then the primary particles started to generate and grew at 140 °C for 72 h, which called the second aging step. An opaque sol was obtained owing to transformation of gel network, and with the repeatedly washing by $NaOH$, HNO_3 and distilled water respectively, TiO_2 nanoparticles were successfully prepared. Chen et al. synthesized TiO_2 particles via a vapour hydrolysis system without mixing. In this process, TiO_2 crystallites nucleated in the matrix to form the primary particles firstly, and further developed to larger particles with increasing temperature (Fig. 2a) [49]. In continuous water vapour hydrolysis system, water vapour was generated at 70 °C, then the hot vapour got into the next container carried by Ar gas and was condensed on the surface of cold solution of titanium tetraisopropoxide (TTIP). Thus, the hydrolysis was expected to occur in the thin interface between water and TTIP after 8 h reaction. As clearly shown in Fig. 2b and c, TiO_2 was made up of secondary particles composed of primary nanoparticles. Li et al. have successfully prepared TiO_2 nanoparticles at different temperatures in a micro-emulsion-mediated hydrothermal process, and TiO_2 with large crystallite size and high crystallinity was synthesized as hydrothermal temperature increasing [50]. In addition, the morphology of TiO_2 changed gradually from spherical to rod-like with the increasing temperature. In this paper, hydrothermal method was combined with reverse micelle synthesis in order to obtain anatase-type titania with high crystallinity. Rui et al. and co-workers have successfully synthesized TiO_2 microspheres assembled by single crystalline rutile TiO_2 nanorods in one-step solvothermal method [51]. The diameters of these microspheres could be easily controlled just by varying the volume of distilled water from 1 to 5 ml, which resulted in decreasing diameters of prepared microspheres from 1 to 5 μm respectively.

2.2.2. 1D TiO_2 nanotubes and nanowires

1D TiO_2 nanostructure seem to be more popular owing to higher photocatalytic activity and lower charge recombination than nanoparticles. Importantly, nanotube played key roles in enhancing light absorbance via multiple reflections and inhibiting photoelectron-hole recombination via acceleration of electron conduction. Bian et al. prepared porous TiO_2 nanotubes by solvothermal alcoholysis [52]. As is shown in Fig. 3a, a mixture consisting of $TiOSO_4$, organic solvents and CNTs template was firstly prepared. With the solvothermal alcoholysis of $TiOSO_4$ at 110 °C for 48 h, nanoscale pieces of the TiO_2 were