



A novel “gel–sol” strategy to synthesize TiO₂ nanorod combining reduced graphene oxide composites



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ABSTRACT

In this study, a novel so-called “gel–sol” process is firstly reported for synthesis of TiO₂ nanorod (TN) combining reduced graphene oxide (RGO) composites. By utilizing the triethanolamine (TEOA) as shape controller and under specific conditions (such as pH=12), the hybrid composites can be readily obtained. The higher pH value benefits the deprotonation of TEOA for adsorption to the stationary nuclei. Therefore, the synthesized hybrid composites have the morphology of crystalline anatase TiO₂ nanorods anchored into the surface of reduced graphene oxide. The hybrid composites fabricated by the novel process have distinct advantages over the traditional methods for obtaining TiO₂ and graphene-based composites in terms of the well-confined TiO₂ morphology and the formation of Ti–C bonds between TN and RGO simultaneously.

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1. Introduction

Carbonaceous materials have been widely utilized for modifying semiconductors for effectively transporting electrons [1,2]. As the emerging carbon-based derivatives, graphene has superior mechanical flexibility, large surface area and excellent electrical conductivity [3,4]. Theoretically, graphene with tunable redox properties has great potentials for enhancing the performance of semiconductors. On the other hand, TiO₂ suffering from the low efficiency and narrow light response range is the typical semiconductor which has been widely studied. The architectural combination of graphene and TiO₂ has been considered as the most exciting idea to produce the next-generation hybrid materials with the high performance. Up to now, various strategies have been explored for fabricating high performance TiO₂/graphene hybrids, which include the simple mixture/sonication [5–7], self-assembling [8,9], hydrothermal [10–12], solvothermal [13–15] and sol–gel processes [16]. These approaches have generally produced TiO₂/graphene hybrid materials which have weak interactions (chemical bonds) among graphene and TiO₂ and no well-defined nanostructure of TiO₂. In fact, the formation of chemical bonds between graphene-based materials and TiO₂ and the nanostructure of TiO₂ particles are crucial for practical applications [17].

Therefore, the new strategy is urgently required for developing advanced TiO₂/graphene hybrid materials.

For the first time, TiO₂ nanorod/reduced graphene oxide (TNGRO) hybrid materials are synthesized by a novel “gel–sol” process which is contrast with the traditional sol–gel approach [18]. With the aid of shape controllers of triethanolamine (TEOA) during the gel–sol process [19], the well-defined TiO₂ nanorod (TN) with the large aspect ratio can be obtained and TNGRO can be formed by incorporation of graphene oxide. The basic process is investigated and the synthesized TNGRO is characterized.

2. Experimental

Graphene oxide (GO) was prepared by the modified Hummers method [20]. In a typical gel–sol process for synthesizing TNGRO, a variable amount of GO was dispersed in 40 mL distilled water under sonication. Then, 40 mL aqueous stock solution by mixing triethanolamine (TEOA) with titanium (IV) isopropoxide (TIPO) at a molar ratio of [TEOA]:[TIPO]=2:1, was added. After adjusting pH value to 12 by adding NaOH solution under vigorous stirring, the mixed solution was transferred into a 100 mL Teflon lined stainless steel autoclave, and aged at 110 °C for 24 h, 150 °C for 72 h and 190 °C for 24 h, respectively. The products were collected by centrifugation, washed with water and ethanol, and then treated in nitrogen at 400 °C for 2 h. The obtained TNGRO is ready for characterizations. Pure TiO₂ nanorods were prepared with the similar procedure. Wide-angle X-ray diffraction (WAXD) spectra

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were recorded using a RINT D/MAX-2500/PC XRD instrument. X-ray photoelectron spectroscopy (XPS) was carried out by an AXIS ULTRA DLD spectrometer (SHIMADZU, Japan). Transmission electron microscopy (TEM) was performed on a FEI, Tecnai G2 F30 (USA) electron microscope.

3. Results and discussion

Fig. 1 has illustrated the gel–sol process for TNRGO synthesis. By controlling the hydrolysis of precursor, the condensed and viscous gel can be formed at 110 °C which acts as both the matrix for particle growing with inhibited coagulation and the reservoir of metal and hydroxide ions for controlled release. During the following sol formation at 150 °C, TEOA containing amino groups can limit the growing rate of the planes parallel to the *c*-axis of TiO₂ tetragonal crystal system as the shape controller according to the specific affinity to produce the rod-like TiO₂ architecture [19]. When GO is incorporated into the system, the further high

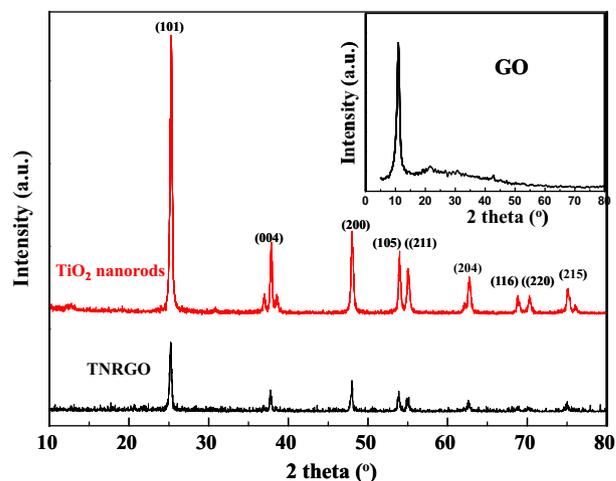


Fig. 3. XRD pattern of TiO₂ nanorods and TNRGO.

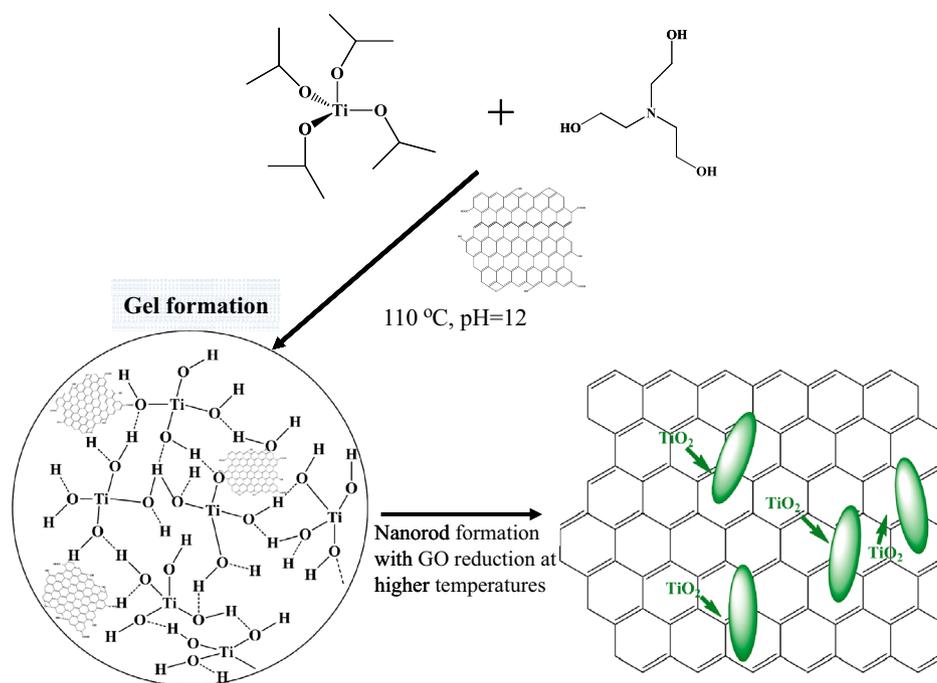


Fig. 1. Evolution for TNRGO formation during the gel–sol process.

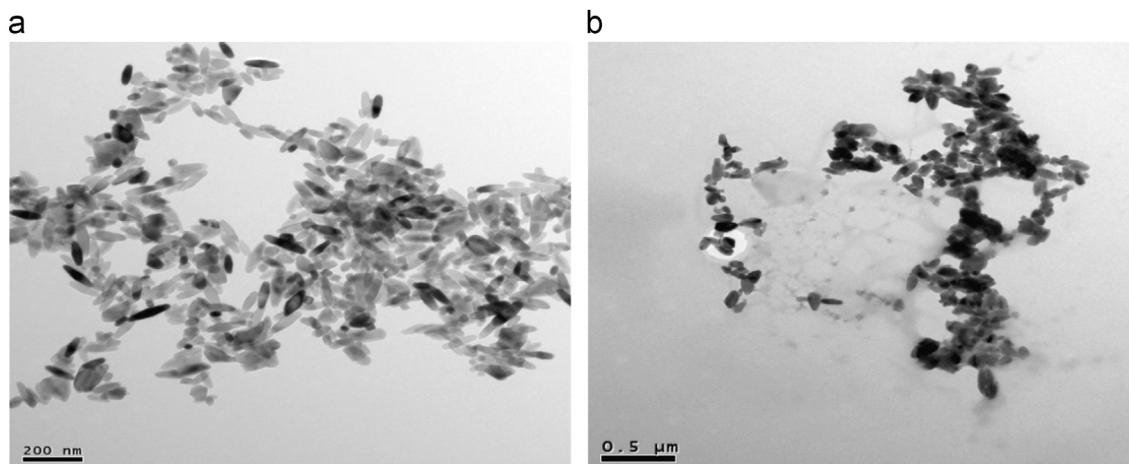


Fig. 2. TEM morphologies of (a) TiO₂ nanorods and (b) TNRGO.

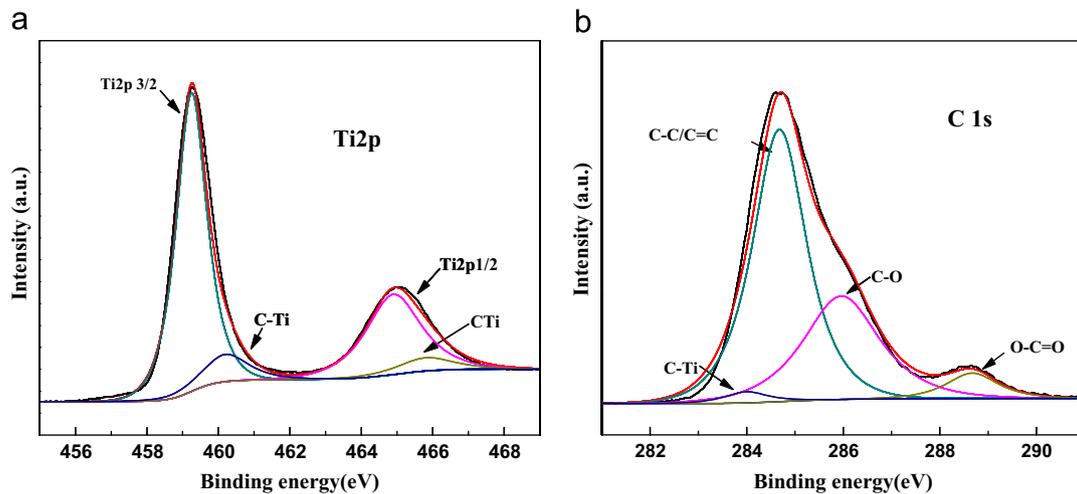


Fig. 4. XPS curve fitting of (a) Ti2p and (b) C1s peaks in TNRGO.

temperature treatment at 190 °C and 400 °C can facilitate bonding formation among GO and TiO₂, reduce the GO and tune the crystalline structure of TiO₂.

The morphologies by TEM observation have been demonstrated in Fig. 2. According to Fig. 2(a), TiO₂ nanorods have been successfully prepared by the gel–sol method at pH=12, and the shape and size of the nanorods are well uniform. TiO₂ nanorods exhibit average dimensions of 150 nm (length) × 30 nm (diameter) (L/D ratio=5). The large aspect ratio of TiO₂ nanorods synthesized by this procedure is the distinct advantage. In fact, several pH values have been investigated and the best nanorod morphology can be obtained at pH value of 12. The higher pH value benefits the deprotonation of TEOA for adsorption to the stationary nuclei. Therefore, the well-confined structure of TiO₂ is generated. Fig. 2 (b) illustrates that TiO₂ nanorods anchored into the surface of graphene oxide which proves that TNGRO hybrid materials have been obtained, which can be further confirmed by XPS.

XRD is utilized to explore the crystalline structures. According to Fig. 3, GO shows the peak at 10.9° is corresponding to the interlayer spacing of 8.11 Å [21] which indicates that GO have been exfoliated successfully. The XRD patterns of TiO₂ nanorods and TNRGO are similar while the intensity of TNRGO is lower than that of TiO₂ nanorods. Both of them have the peaks at 25.3° (101), 37.9° (004), 48.1° (200), 54° (105, 211), 62.7° (204), 69.1° (116, 220) and 75° (215) which illustrates the anatase phase of TiO₂. Interestingly, there is no GO peak in TNRGO. This phenomena may illustrate that GO have been at least partially reduced into graphene under the gel–sol process. The disappearance of diffraction peak ($2\theta=24.5^\circ$) belonging to graphene is possibly due to overlapped with (101) TiO₂ peak and low content of graphene in hybrid materials [22]. Therefore, the gel–sol approach in this study can produce TiO₂ nanorods with the anatase phase and partially reduce GO simultaneously.

Furthermore, XPS results of TNRGO are shown in Fig. 4. According to Fig. 4(a), the deconvolution of Ti2p peak of TNRGO can obtain four fitting curves at 464.5 eV, 458.9 eV, 460.2 eV and 465.8 eV. The curves at 464.5 eV and 458.9 eV are assigned to the Ti2p 1/2 and Ti2p 3/2. The curves at 460.2 eV and 465.8 eV are assigned to the Ti–C bond [23]. This proves that the chemical bonds among RGO and TiO₂ nanorods have been formed during the process in this study. Formation of Ti–C bonds can also be found by the deconvolution of C1s peak. Fig. 4(b) shows the deconvolution of C1s peak which has four fitting curves centered at 283.8 eV, 284.8 eV, 286.2 eV and 288.8 eV. The curve at 283.8 eV is corresponding to Ti–C bond [23], and the curves at 284.8 eV, 286.2 eV and 288.8 eV are assigned to the C–C/C=C, C–O, and O–C=O bonds respectively [24]. TNRGO hybrid materials

fabricated by the novel process have distinct advantages over the traditional methods for obtaining TiO₂ and graphene-based mixtures in terms of the well-confined TiO₂ morphology and the formation of chemical bonds among TN and RGO.

4. Conclusions

TNRGO hybrid materials have been successfully synthesized by the novel gel–sol method. XRD proves that the anatase phase of TiO₂ nanorods in TNRGO has been formed and GO have been reduced during this process. TEM discloses the well-defined nanorod morphology of TiO₂ with the large aspect ratio which can be perfectly anchored into the surface of RGO. XPS results have testified that the bonds of Ti–C are formed in TNRGO which definitely benefits potential applications of the hybrid materials in various fields.

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