Graphene Oxide Regulated Tin Oxide Nanostructures: Engineering Composition, Morphology, Band Structure, and Photocatalytic Properties

Xiaoyang Pan and Zhiguo Yi*

Key Laboratory of Design and Assembly of Functional Nanostructures & Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

* Supporting Information

ABSTRACT: A facile, one-step hydrothermal method has been developed to fabricate tin oxide−reduced graphene oxide (Sn−RGO) nanocomposites with tunable composition, morphology, and energy band structure by utilizing graphene oxide (GO) as a multifunctional two-dimensional scaffold. By adjusting the GO concentration during synthesis, a variety of tin oxide nanomaterials with diverse composition and morphology are obtained. Simultaneously, the varying of GO concentration can also narrow the bandgap and tune the band edge positions of the Sn−RGO nanocomposites. As a result, the Sn−RGO nanocomposites with controllable composition, morphology, and energy band structure are obtained, which exhibit efficient photoactivities toward methyl orange (MO) degradation under visible-light irradiation. It is expected that our work would point to the new possibility of using GO for directing synthesis of semiconductor nanomaterials with tailored structure and physicochemical properties.

KEYWORDS: graphene oxide, tin oxide, visible-light photocatalysis, morphology control, composition modulation

1. INTRODUCTION

Recent years have witnessed an ever-growing interest in fabrication of metal oxide semiconductor photocatalysts with desirable morphologies and distinct structures, due to their structure-dependent optical, electrical, and catalytic properties.1−6 In particular, the synthesis of tin oxide (SnO2, SnO, and so on) nanostructures for solar energy conversion has been gaining immense attention.7−14 It is reported that the construction of tin oxide with desirable architectural structure, such as one-dimensional (1D) nanorods, 2D nanosheets, or 3D hierarchical nanostructures, would be beneficial for high light-collection efficiency and fast charge carriers transport,15 which provides an effective strategy for improving the photoactivities of tin oxides.16−19 Unfortunately, the reported synthesis of tin oxide with tunable nanostructures often requires multistep synthetic procedures involving the manipulation of a variety of experimental parameters, which is time-consuming and less productive.20,21

In addition to controlling the morphology of tin oxides, the introduction of graphene to fabricate tin oxide−graphene (Sn−GR) nanocomposites has also been demonstrated as an effective strategy to enhance their performance.22−24 However, despite numerous efforts on synthesis of tin oxide nanostructures, tin oxides in most of the Sn−GR hybrids are in the form of simple nanoparticles.25−30 Although several reports have successfully grown SnO2 nanorods/nanosheets onto GR substrate,31−34 the organic structure-directing agents are often required during the synthetic procedure, which can strongly adsorb onto the surface of SnO2 and block the surface active sites for photocatalytic reactions.35,36

Notably, as the mostly investigated tin oxide photocatalysts, SnO2 and SnO can only be activated by UV light irradiation, which accounts for only 4% of the solar spectrum, due to their intrinsically wide bandgap.37,38 Therefore, band structure engineering strategy needs to be utilized for enhancing the visible-light absorption of tin oxide photocatalysts. More importantly, considering that design strategy alone leads to only limited improvement of the photocatalyst, it is highly desirable to develop Sn−GR nanostructures which integrate all of the aforementioned design principles. However, it is still a significant challenge to achieve this goal by a simple and one-step process without organic species since simultaneously control of these factors generally requires organic structure-directing agents, time-consuming synthetic steps, and complex experimental parameters manipulation.

Herein, we highlight a facile and one-step strategy by utilizing graphene oxide (GO) as a multifunctional 2D scaffold to realize composition modulation, morphology control, and band structure engineering of tin oxides without organic species. Our inspiration is derived from the following idea: As the most...
often used precursor for GR. GO with abundant oxygenated groups would provide multivalent interaction or even involve in the redox reaction with the metal ions precursors of semiconductors. Therefore, it is possible to use GO for tuning the relative amount of Sn\textsuperscript{2+} and Sn\textsuperscript{4+} ions in the resulting tin oxides through the redox reaction between Sn\textsuperscript{2+} and GO. Moreover, the composition modulation of tin oxide by GO would in turn engineer their energy band structures. Considering that the functional group on GO also plays a key role in nucleation and growth of nanomaterials, we could also utilize GO to control the morphology of tin oxides. As a result, a variety of visible-light-driven photocatalysts: Sn\textsubscript{3}O\textsubscript{4}, Sn\textsubscript{O} (Sn\textsuperscript{2+} doped)/RGO and ternary Sn\textsubscript{2}O\textsubscript{3}/Sn\textsubscript{O} \textsubscript{2}/RGO with diverse morphology and band structure are obtained by simply changing the GO concentration during synthesis.

2. EXPERIMENTAL SECTION

Materials. Tin(II) fluoride (SnF\textsubscript{2}), tin fluoride (SnF\textsubscript{3}), tin(II) chloride dehydrate (SnCl\textsubscript{2}), anhydrous ethanol (EtOH), phosphorus pentoxide (P\textsubscript{2}O\textsubscript{5}), hydrochloric acid (HCl), graphite powder, potassium persulfate (K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}), hydrogen peroxide (30\%H\textsubscript{2}O\textsubscript{2}), potassium permanganate (K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}), sodium hydroxide (NaOH), sodium fluoride (NaF), potassium dichromate (K\textsubscript{2}CrO\textsubscript{7}), benzaldehyde (C\textsubscript{6}H\textsubscript{5}CHO), benzoic acid (C\textsubscript{6}H\textsubscript{5}COOH), and sodium sulfate (Na\textsubscript{2}SO\textsubscript{4}) were purchased from Sinopharm Chemical Regent Co., Ltd. (Shanghai, China). Deionized water was supplied from local sources. All of the materials were used as received without further purification.

Synthesis. Graphene oxide was synthesized from graphite powder according to the modified Hummers method (for details see the Supporting Information).

Characterization. The crystal structures of the as-prepared samples were analyzed on a Rigaku Miniflex II X-ray diffractometer with Cu K\textalpha\ radiation. The optical properties of the samples were characterized by a Cary 500 UV–visible ultraviolet/visible diffuse reflectance spectrophotometer (DRS), during which BaSO\textsubscript{4} was employed as the internal reflectance standard. A field-emission scanning electron microscope (JSM-6700F) and transmission electron microscope (JEM-2010, FEI, Tecnai G\textsuperscript{2} F20 FEG TEM) were used to determine the morphology and microscopic structure of the as-synthesized samples. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific ESCA Lab250 spectrometer which consists of a monochromatic Al K\textalpha\ X-ray source, a hemispherical analyzer, and sample stage with multiaxial adjustability to obtain the composition on the surface of samples. All of the binding energies were calibrated by the C 1s peak of the surface adventitious carbon at 284.6 eV. Photoluminescence analysis was carried out with a Varian Cary Eclipse spectrometer at an excitation wavelength of 325 nm.

Photo-electrochemical Measurements. The photo-electrochemical analysis was carried out in a conventional three-electrode cell. A Ag/AgCl electrode was used as reference electrode and Pt electrode acted as the counter electrode. Fluoride–tin oxide (FTO) glass was used to prepare the working electrode, which was first cleaned by ultrasound in ethanol for 30 min and dried at 80 °C. The sample powder (10 mg) was ultrasonicated in 1 mL of anhydrous ethanol to obtain an evenly dispersed slurry. Then, the slurry was spreaded onto the FTO glass whose side part was protected in advance using Scotch tape. The working electrode was dried overnight under ambient conditions. A copper wire was connected to the side part of the working electrode using a conductive tape. Uncoated parts of the electrode were isolated with epoxy resin. The exposed area of the working electrode was 0.25 cm\textsuperscript{2}. The irradiation source was a 300 W Xe lamp (CEL-HXF300) system with UV-CUT filter (λ > 420 nm). The photocurrent measurements and Mott–Schottky analyses were performed in a homemade three-electrode quartz cell with a CHI660D workstation. The electrolyte was 0.2 M aqueous Na\textsubscript{2}SO\textsubscript{4} solution (pH = 6.8) without additive.

Photocatalytic Activities. For photocatalytic degradation methyl orange (MO), 30 mg of photocatalyst was dispersed into 60 mL of MO solution (20 ppm) in a quartz vial. The resulting suspension was stirred in the dark for 1 h to ensure the establishment of an adsorption–desorption equilibrium between the sample and reactant. Then the reaction system was irradiated by a 300 W Xe lamp (CEL-HXF300) system with UV-CUT filter (λ > 420 nm). As the reactions proceed, 3 mL of the suspension was taken at a certain time interval and was centrifuged to remove the catalyst. Afterward, the residual amount of MO in the solution was analyzed on the basis of its characteristic optical absorption at 470 nm, using a UV/vis/near-IR spectrophotometer (PerkinElmer Lambda 900) to measure the change of MO concentration with irradiation time based on Lambert–Beer’s law. The percentage of degradation is denoted as C/C\textsubscript{0}. Here C\textsubscript{0} is the absorption of MO solution at each irradiation time interval of the main peak of the absorption spectrum, and C\textsubscript{0} is the absorption of the initial concentration when the absorption–desorption equilibrium was achieved.

3. RESULTS AND DISCUSSION

The synthesis of the tin oxide and tin oxide reduced graphene oxide nanocomposites (Sn–RGO) is achieved by a facile one-step hydrothermal method using SnF\textsubscript{2} and GO (Supporting Information Figures S1–S3) as precursors. As shown in Figure 1a, blank tin oxide synthesized from hydrothermal treatment of
SnF₂ solution is mixed-valence Sn₃O₄. All of the diffraction peaks match the standard pattern of a triclinic Sn₃O₄ structure (JCPDS 16-0737). The Sn–RGO nanocomposites with low RGO contents (1, 2, and 5%) exhibit XRD patterns similar to that of blank Sn₃O₄ (Supporting Information Figure S4a). When the RGO content increased to 10% (Sn–RGO-10%), some new diffraction peaks corresponding to SnO₂ emerged and dominated the XRD patterns (Supporting Information Figure S4b). When RGO content reached 20%, all of the diffraction peaks of Sn–RGO nanocomposite (Sn–RGO-20%) could be assigned to the rutile SnO₂.

Raman spectroscopy analysis further confirms the phase transformation from Sn₃O₄ to SnO₂ in the presence of GO. As shown in Supporting Information Figure S5, Sn₃O₄ features the Raman peaks at 143 and 170 cm⁻¹, RGO features the Raman peaks at 1344 and 1596 cm⁻¹, whereas SnO₂ features the Raman peaks at 600 cm⁻¹. The evolution of Raman modes of the Sn–RGO composites have clearly shown that the introduction of GO can modulate the composition of tin oxide to obtain (Figure 1b): Sn₃O₄, binary Sn₃O₄–RGO (Sn–RGO-1%, Sn–RGO-2%, and Sn–RGO-5%), ternary Sn₃O₄/SnO₂/RGO (Sn–RGO-10%), and binary SnO₂/RGO (Sn–RGO-20%).

Accompanying the changes of composition and structure of the tin oxides, morphology of the as-obtained Sn–RGO nanocomposites is modulated as well. The blank Sn₃O₄ shows a flower-like morphology composed of Sn₃O₄ nanosheets, as shown in Figure 2a. Sn–RGO-1% and Sn–RGO-2% samples have hierarchical structures, in which Sn₃O₄ nanosheets are vertically grown on the RGO surface (Figure 2b,c). For the Sn–RGO-5%, both Sn₃O₄ nanosheets and nanoparticles coexist on the surface of RGO (Figure 2d), while for Sn–RGO-10% and Sn–RGO-20%, the RGO surface is densely covered by mostly SnO₂ nanoparticles (Figure 2e,f). These results indicate that the introduction of GO can tune the growth and assembly of tin oxide nanosheets and the morphology of the tin oxide can be further tuned by varying the addition amount of GO.

Figure 2. SEM images of the Sn₃O₄ (a). Tin oxide reduced graphene oxide nanocomposites (Sn–RGO-x%): Sn–RGO-1% (b), Sn–RGO-2% (c), Sn–RGO-5% (d), Sn–RGO-10% (e), and Sn–RGO-20% (f). Here x denotes the weight ratio of RGO.

Figure 3. TEM (a) and HRTEM (b) images, EDX spectrum (c), and XPS spectrum (d) of Sn–RGO-2%.

To further identify the microscopic morphology and structure of the Sn–RGO nanocomposite, Sn–RGO-2% sample is investigated by TEM analysis. As shown in Figure 3a, Sn₃O₄ nanosheets are mostly grown upright with a random orientation on the RGO support, which is consistent with the aforementioned SEM observation. The thickness of the Sn₃O₄ nanosheets is determined to be ca. 9 nm. The RGO layers can also be clearly identified in the edge area of Sn–RGO nanostructures (Figure 3a). The high resolution TEM (HRTEM) image in Figure 3b displays a single Sn₃O₄ nanosheet with distinct lattice fringes of 0.334 nm, which is attributed to the (111) plane of the Sn₃O₄. The corresponding EDX spectrum (Figure 3c) of Sn–RGO-2% confirms the element composition of C, O, and Sn.

X-ray photoelectron spectroscopy (XPS) is utilized to investigate the chemical states of Sn–RGO nanocomposite. The survey spectrum of Sn–RGO-2% shown in Supporting Information Figure S6a further confirms the existence of Sn, O, and C. The high resolution spectrum of C 1s (Supporting
Information Figure S6b) reveals that the oxygenation species on the GO are remarkably reduced in comparison to the original GO (Supporting Information Figure S7). This result indicates that the original GO is effectively converted to reduced GO (RGO) during the synthesis of the Sn−RGO nanocomposites. The two characteristic peaks at 530.4 and 531.9 eV shown in the O 1s spectra can be assigned to the Sn−O and hydroxyl species, respectively (Supporting Information Figure S6c). The prominent peak of Sn 3d shown in Figure 3d can be deconvoluted into two subpeaks centered at 486.3 and 487.0 eV, which is assigned to the Sn 2+ and Sn 4+, respectively.41

Figure 4a shows the UV−vis diffuse reflectance spectra (UV−vis DRS) of the samples. It is shown that the Sn3O4 exhibits obvious visible-light absorption with a band gap of 2.75 eV (Figure 4b). As compared to Sn3O4, Sn−RGO nanocomposites show obviously enhanced visible-light absorption in the range of 500−800 nm, which can be attributed to intrinsic absorption of black colored graphene.45−47 The band gaps of the Sn−RGO samples are determined based on the Tauc plots shown in Supporting Information Figure S8. The results show that the RGO decoration narrows the band gap of the tin oxide. This can be attributed to the electronic interaction between tin oxide and RGO, which is also observed on other metal oxides−RGO nanocomposites.48−50

By using the Mott−Schottky analysis (Figure 4c and Supporting Information Figure S9), the band edge positions of the samples are determined (Figure 4d and Supporting Information Table S1). For Sn3O4, its conduction band minimum is determined to be −0.94 V vs NHE and the corresponding valence band maximum is calculated to be +1.81 V vs NHE. With the increase of RGO weight content, a positive shift of the Sn3O4 conduction band of Sn3O4−RGO nanocomposites (Sn−RGO-1%, -2%, -5%) is realized. It is reported that Sn2+ cations in Sn3O4 and SnO are responsible for more negative conduction bands than that of SnO2.51 Therefore, the positive shift of the Sn3O4 conduction band can be explained by the decrease of Sn2+ cations in the Sn−RGO nanocomposites, which is caused by the redox reaction between Sn2+ and GO. As compared to the Sn−RGO nanocomposites with relatively low RGO content, Sn−RGO-10% and Sn−RGO-20%, in which the primary component is SnO2, possess more positive conduction band minima. This can be ascribed to the more positive conduction band of SnO2 when compared to Sn3O4.51 These results indicate that the introduction of GO can effectively engineer the energy band structure (band gap narrowing and band edge position tuning) of tin oxide in the resultant Sn−RGO nanocomposites.

Notably, although SnO2 is a wide band gap semiconductor (3.4 eV), the band gap of SnO2 in Sn−RGO-20% is narrowed to 2.69 eV (Supporting Information Figure S8e). The band gap narrowing of SnO2 may be attributed to two possible reasons: one is the result of electronic interaction between RGO and SnO2.50 The other is band gap narrowing of SnO2 by Sn2+ doping,7 since Sn2+ is used as a precursor, and not all of them are oxidized to Sn4+. To examine what reason is accounted for the band gap narrowing of SnO2, we have then prepared SnO2 and SnO2−RGO-20% samples (Supporting Information Figure S10) using SnF4 and GO as precursors with the same procedures for preparing the Sn−RGO nanocomposites. The UV−vis DRS analysis (Supporting Information Figure S11) indicates that the band gap narrowing of SnO2 in Sn−RGO-20% is mainly ascribed to aliovalent Sn2+ doping. This is further confirmed by XPS analysis (Supporting Information Figure S12). It is worth noting that the ion radius of Sn2+ (0.62 Å) is similar to that of Sn4+ (0.69 Å).52 Therefore, Sn2+ doping in the SnO2 nanostructure is more favorable on preserving the intrinsic crystal structure and thus decreasing the charge recombination centers.

Figure 4. UV−vis diffuse reflectance spectra (DRS) (a), Tauc plots of Sn3O4 (b), Mott−Schottky plot of Sn3O4 (c), and band edge positions (d) of the Sn3O4 and tin oxide reduced graphene oxide nanocomposites (Sn−RGO-x%). Here x denotes the weight ratio of RGO.
From the preceding results, it is clearly seen that the addition of GO during the synthetic procedure has a significant effect on engineering the composition, morphology, and energy band structure of the tin oxides. To clarify the underlying mechanism, a variety of controlled experiments have been carried out. First, the mechanism of composition modulation by GO is investigated. From the aforementioned results, we can conclude that the phase transformation from SnO4 to SnO2 occurred in the presence of GO, indicating that GO addition would facilitate the oxidation of Sn2+ into Sn4+ during the synthesizing procedure. This can be explained by the redox reaction between Sn2+ and the oxygenated groups on GO, in which the Sn2+ is oxidized to Sn4+ while the oxygenated groups on GO are consumed.26,27 To further examine this point, graphene (GR) with almost no oxygenated functional groups has been used to fabricate tin oxide–graphene nanocomposite (Sn–GR-20%), it can be seen that the Sn–GR-20% possesses the same XRD patterns as the blank SnO2 indicating that GR without oxygenated groups cannot modulate the composition of tin oxide (Supporting Information Figure S13).

In addition, it should be noted that the dissolved oxygen can also oxidize Sn2+ to Sn4+ during the synthesis.38 As a result, in the absence of GO, part of the Sn2+ ions are oxidized by dissolved oxygen and thus a mixed-valence Sn3O4 is obtained. In the presence of GO, the dissolved oxygen and GO both contribute to the oxidation of the Sn2+ and thus most of the Sn2+ are oxidized to Sn4+. Thus, the composition modulation of tin oxide by GO can be explained by the following equations:

\[
3SnF_2 + 3H_2O + \frac{1}{2}O_2 \rightarrow Sn_3O_4 + 6HF \\
SnF_2 + GO + H_2O + \frac{1}{2}O_2 \rightarrow SnO_2 + RGO + 2HF
\]

It should be noted that a small amount of GO is insufficient to change the bulk composition of tin oxide (Sn–RGO-1%, -2%, and -5%). Therefore, Sn–RGO nanocomposites (Sn–RGO-10% and -20%) with SnO2 as primary component can only be obtained at higher GO concentration. Moreover, the involvement of F− is also important. If the raw material SnF2 is replaced by SnCl2, only SnO2–RGO composite materials can be obtained.26,27 This is because when SnCl2 is used as precursor, the Sn2+ will be oxidized easily to Sn4+ and then hydrolyzed to form SnO2. In contrast, the F− ions in SnF2 can retard the oxidation of Sn2+ and thus SnO2 is obtained during hydrothermal treatment.41 With the addition of GO, the oxygenated groups on it endow GO with oxidizing capacity to facilitate the oxidation of Sn2+. Therefore, the combination of GO and F− ions have enabled flexible control of tin oxide composition.

To investigate the role of the GO on controlling the morphology of tin oxide nanostructures, the formation process of the Sn–RGO nanocomposites has been further studied by time-dependent experiments. As displayed in Supporting Information Figure S14a, the samples with time duration of 1 h are RGO sheets with small nanoparticles on their surface. With the reaction proceeding to 6 h (Supporting Information Figure S14b), a large amount of small particles are decorated on the surface of the RGO sheets while a small number of tin oxide nanosheets emerge. With a longer reaction time of 12 h, the surface of the RGO substrate is almost covered by the tin oxide nanosheets while tin oxide nanoparticles can still be observed on the surface of RGO (Supporting Information Figure S14c).

After reaction for 24 h, the RGO surface is completely covered by the tin oxide nanosheets (Supporting Information Figure S14d).

Furthermore, the formation mechanism of the tin oxide nanosheets is also investigated. As shown in Supporting Information Figure S15, the result that only irregular nanoparticles are obtained when SnCl2 is used as precursor suggests that the F− ions derived from SnF2 precursor play an important role on directing the growth of 2D sheet-like morphology. F− ions would favorably interact with the tin oxide surface and thus facilitate the formation of the 2D structure with specific exposed facets.38

Based on the aforementioned results, the growth mechanism of tin oxide nanosheets on the RGO surface at low GO content is proposed as follows: At the initial stage, Sn2+ ions tend to adsorb on the negative charged GO surface (−38 mV, Supporting Information Figure S16) while F− ions with negative charge could not access the GO surface due to electrostatic repulsion.42 Therefore, only particle-like tin oxide is formed on the surface of GO at the initial stage (Scheme 1).

**Scheme 1. Schematic Illustration of the Growth Mechanism of Tin Oxide Nanosheets on RGO Surface at Low GO Concentration:** (a) Sn2+ Ions Adsorbing onto the Negatively Charged GO Surface; (b) Growth of Tin Oxide Nanoparticles on the Surface of GO and Consumption of Oxygenation Functional Groups on GO; (c–e) Heterogeneous Nucleation and Growth of Tin Oxide Nanosheets

During this process, the Sn2+ ions could react with the oxygenated functional groups on GO and result in the removal of these functional groups on GO. Since the negative charge of GO is derived from these functional groups,39 the removal of these groups and the adsorption of Sn2+ ions on it would result in a positively charged RGO surface, which would favor the adsorption of F− ions. As a result, the residual Sn2+ and F− ions in the solution would subsequently interact with the tin oxide nanocrystals on RGO and grow into 2D nanostructure through surface fluorine passivation.

Considering that the morphology of tin oxide is also influenced by the pH values,8 the possibility of GO on changing the pH values of the reaction solution is also examined. For the SnF2 aqueous solution, the pH value is determined to be 3.00, owing to the hydrolysis of SnF4+. With the addition of GO, the pH value of the solution is almost constant (2.97). Therefore, the morphology evolution of tin oxide from nanosheets to nanoparticles in the presence of GO can be explained as follows (Supporting Information Scheme S1): With the increase of the GO concentration in the reaction...
To understand which group is more active for structure separation,55 which can be evidenced by the photo-luminescence (PL) analysis. As shown in Figure 5a, blank SnO₂ emits a broad PL emission centered at ca. 450 nm, which can be attributed to the charge recombination near the band gap. In contrast, Sn−RGO-2% exhibits almost no PL emission, indicating more efficient charge separation over Sn−RGO-2%.59

Photoelectrochemical analysis is further performed to prove the role of RGO on promoting the charge separation over the Sn−RGO nanocomposites. As shown in Figure 5b, under the visible-light irradiation, the photocurrent of the Sn−RGO-2% is much higher than that of SnO₂, indicating more efficient charge separation over Sn−RGO-2% than SnO₂.58,59 The increased photocurrent of Sn−RGO-2% with the increase of the irradiation time is attributed to the fact that no sacrificial agent for photogenerated hole is used in the photovoltaic experiments. Under the irradiation of visible light, the electrons photogenerated from tin oxide are transferred to the Pt electrode, and the photogenerated holes are accumulated in the valence bands of tin oxides since they cannot be scavenged by the water molecule (please note zero bias voltage is applied in the experiment). The accumulation of holes will result in the decrease of photocurrent with time. The enhanced charge carrier transfer can also be evidenced by electrochemical impedance spectroscopy (EIS) analysis. As compared to SnO₂, the SnO₂-RGO-2% suggests a faster charge−carrier transfer rate in SnO₂-RGO-2%.58

As a result, the Sn−RGO nanocomposites with tunable composition, morphology, and energy band positions as well as efficient charge separation may act as promising candidates for solar energy conversion. As a proof-of-concept, we take photocatalytic methyl orange (MO) degradation as a typical example to demonstrate the application of Sn−RGO nanocomposites. As shown in Figure 5d and Supporting Information Figure S19, the SnO₂-RGO nanocomposites with low RGO content (1%, 2%, and 5%) exhibit obviously enhanced photocatalytic performance as compared to that of SnO₂ under visible-light irradiation (λ > 420 nm). In particular, the Sn−RGO-2% nanocomposite shows the best photoactivity,
which can completely decompose MO within 4 min (Figure Sd and Supporting Information Figure S20).

Since the bulk compositions of Sn−RGO-10% and Sn−RGO-20% (SnO2 as the primary component) are different from the other samples, their photoactivities are compared to the SnO2−RGO composites prepared using SnF2 and GO as precursors (Supporting Information Figures S10 and S11). As shown in Supporting Information Figure S21, the Sn−RGO-20% with Sn2+ doping shows much higher activity than that of SnO2−RGO-20% without Sn2+ doping toward MO degradation under visible-light irradiation. These results show unambiguously the dominant role of compositional modulation on the photoactivity. The fact that Sn−RGO-20% shows lower photoactivity than Sn−RGO-10% (Supporting Information Figure S21) can be attributed to two reasons: One is the decreased concentration of tin oxide photoactive component as well as the increased light shielding effect of black RGO.39,60 The other involves synergistic effect between the mixed tin oxide in Sn−RGO-10% considering that it is comprised of SnO2 and SnO, with matched energy band structure (Supporting Information Figure S22). The photogenerated holes of SnO2 would transfer to the valence band of Sn3O4 while the photoexcited electrons of Sn3O4 may also transfer to the conduction band of SnO2.31 As a result, the charge separation efficiency is promoted and thus Sn−RGO-10% shows higher photoactivity than that of Sn−RGO-20%.

To investigate the morphology effect on the photoactivity of tin oxide, we also prepared SnO2 nanosheets (SnO2−NS) using SnCl2 and NaF as precursors (Supporting Information Figure S23a) and prepared SnO2 nanoparticles (SnO2−NPs) using SnCl2 as precursor (Supporting Information Figure S15). All the samples possess a rutile SnO2 phase (Supporting Information Figure S23b) and exhibit identical UV−vis DRS spectra (Supporting Information Figure S23c), implying a same content of Sn2+ doping. Therefore, the distinct photoactivity (Supporting Information Figure S23d) implies the SnO2 nanosheets with specific facets exposure are more active for photocatalytic reaction than that of SnO2 nanoparticles.61

The durability of the catalyst is also investigated. As shown in Supporting Information Figure S24a, from the first to second run there is an obvious decrease of photoactivity; however, the activity remains stable from the second to the fifth run. To clarify the possible reasons, a variety of characterizations have been employed. We first examined the crystal structure of the samples after the photoreaction. As shown in Supporting Information Figure S24b, the crystal structure and crystallinity of tin oxide before and after the reaction remain unchanged. The Raman spectroscopy analysis further reveals no obvious degradation of RGO (Supporting Information Figure S24c).62,63 However, an apparent morphology change of the sample is found after the photocatalytic reaction (Supporting Information Figure S24d). That is, part of the tin oxide nanosheets peeled off from the RGO substrate after the photoreaction. Since the interfacial interaction between tin oxide and RGO is a prerequisite for high efficient charge carriers’ separation,62 the exfoliation of the tin oxide from RGO surface would account for the decrease of the photoactivity.

To determine the quantum efficiency of the Sn−RGO nanocomposite, we perform a photo reduction test of Cr(VI) upon the Sn−RGO-2% sample under visible-light irradiation. As shown in Supporting Information Figure S25, the Sn−RGO-2% sample shows obviously enhanced visible-light photoactivity for Cr(VI) reduction and has a quantum efficiency of 2.04% at 420 nm (Supporting Information Figure S26).64

4. CONCLUSION

In conclusion, graphene oxide (GO) is utilized as a structure-directing agent to control the composition, morphology, and band structure of tin oxide−reduced graphene oxide (Sn−RGO) nanocomposites while neither organic surfactants nor organic solvents have been used. By adjusting the addition amount of GO during synthesis, tin oxide nanostructure in Sn−RGO evolves from hierarchical Sn3O4 nanosheet arrays to ultrathin Sn2+ self-doped SnO2 nanoparticles. The Sn−RGO nanocomposites with narrowed band gap and tunable energy band structure show efficient photocatalytic activities for MO degradation under visible-light irradiation.

It is known that tremendous efforts have been devoted to synthesizing graphene-based nanocomposites for diverse applications. In most cases, graphene oxide is used as precursor for graphene (GR). Notably, during the synthesis of such composite materials, GO is most often introduced merely for the sake of GR without putting it into full play with elaborate design and is unable to utilize the structure advantage of GO. This work provides valuable guidance for further design and synthesis of graphene-based photofunctional materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b07858.

XRD, SEM, and TEM images of graphene oxide, additional XRD patterns, UV−vis diffuse reflectance spectra (DRS), XPS spectra, Tauc plots, Mott−Schottky plots, the energy band gap and conduction band and valence band positions, and additional SEM and TEM images of the samples, a scheme of the morphology evolution mechanism, and photocatalytic performance of the samples. (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: zhiguo@fjirsm.ac.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the National Key Project on Basic Research (Grant No. 2013CB933203), the Natural Science Foundation of China (Grant Nos. 21373224 and 21577143), the Natural Science Foundation of Fujian Province (Grant Nos. 2014H0054 and 2015J05044), and the One Hundred Talents Program of the Chinese Academy of Sciences.

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