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Abstract

"Nano tungsten oxide (WO₃) particles were synthesized on the surface of graphene (GR) sheets by using a simple sonochemical method. The obtained composite, WO₃@GR, was characterized by X-ray diffraction, N₂ adsorption/desorption analysis, thermo-gravimetric analysis, Raman spectroscopy and UV-vis diffuse reflectance spectra measurements. It was found that chemical bonds between the nano WO₃ particles and the GR sheets were formed. The average particle size of the WO₃ was evidenced to be around 12 nm on the GR sheets. When used as photocatalyst for water splitting, the amount of evolved O₂ from water for the WO₃@GR composite with 40 wt% GR inside was twice and 1.8 times as much as that for pure WO₃ and mixed-WO₃/GR, respectively. The excellent photocatalytic property of the WO₃@GR composite is due to the synergistic effects of the combined nano WO₃ particles and GR sheets. The sensitization of WO₃ by GR enhances the visible light absorption property of WO₃@GR. The chemical bonding between WO₃ and GR minimizes the interface defects, reducing the recombination of the photo-generated electron-hole pairs. Furthermore, the GR sheets in the WO₃@GR composite enhance electrons transport by providing low resistance conduction pathways, leading to improved photo-conversion efficiency. The methodology opens up a new way of obtaining photoactive GR-semiconductor composites for photodissociating water under visible light."

Keywords

graphene, water, evolution, oxygen, wo₃, photocatalytic, synthesis, enhanced, composite

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PAPER

Synthesis of WO₃@Graphene composite for enhanced photocatalytic oxygen evolution from water

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Nano tungsten oxide (WO₃) particles were synthesized on the surface of graphene (GR) sheets by using a simple sonochemical method. The obtained composite, WO₃@GR, was characterized by X-ray diffraction, N₂ adsorption/desorption analysis, thermo-gravimetric analysis, Raman spectroscopy and UV-vis diffuse reflectance spectra measurements. It was found that chemical bonds between the nano WO₃ particles and the GR sheets were formed. The average particle size of the WO₃ was evidenced to be around 12 nm on the GR sheets. When used as photocatalyst for water splitting, the amount of evolved O₂ from water for the WO₃@GR composite with 40 wt% GR inside was twice and 1.8 times as much as that for pure WO₃ and mixed-WO₃/GR, respectively. The excellent photocatalytic property of the WO₃@GR composite is due to the synergistic effects of the combined nano WO₃ particles and GR sheets. The sensitization of WO₃ by GR enhances the visible light absorption property of WO₃@GR. The chemical bonding between WO₃ and GR minimizes the interface defects, reducing the recombination of the photo-generated electron–hole pairs. Furthermore, the GR sheets in the WO₃@GR composite enhance electrons transport by providing low resistance conduction pathways, leading to improved photo-conversion efficiency. The methodology opens up a new way of obtaining photoactive GR-semiconductor composites for photodissociating water under visible light.

Introduction

Recently, great interest has been focused on semiconductor photocatalysis utilizing solar energy to photodissociate water.^{1–5} Solar photolysis of water is one of the cleanest ways of producing hydrogen and oxygen, which has great potential in solving energy problem. As a semiconductor for spontaneous photolysis, three main thermodynamic requirements should be fulfilled: (1) its band gap must be higher than water decomposition voltage (1.23 eV); (2) its band edge positions must straddle the hydrogen and oxygen redox potential, and (3) it must be stable against photo corrosion during photocatalysis. Accordingly, semiconductors including TiO₂, WO₃, Bi₂WO₆, ZnO, Bi₂O₃ and CdS *etc.* have been reported to be used in water splitting to produce hydrogen or oxygen.^{6–12} Among them, TiO₂ is the most extensively studied photocatalyst for its low toxicity, long-term thermodynamic stability, high photostability, and high efficiency.^{5,12,13} Unfortunately, TiO₂ is only active in the ultraviolet

light range due to its wide band gap (3.2 eV), result in utilizing only 5% of the total solar spectrum.

Nanostructured tungsten trioxide (WO₃), as one of the n type semiconductors with a band gap of 2.8 eV, has attracted a lot of interests in photocatalysis because of its strong adsorption within the solar spectrum (≤ 500 nm), stable physicochemical properties as well as its resilience to photo corrosions.^{7,14–16} Under the irradiation of visible light, photoinduced electrons and holes can be produced in the conduction band and valence band of WO₃, respectively. The photo generated holes can be used to drive the water-splitting reaction to produce oxygen. Generally, nanocrystalline semiconductors have poor charge mobility and thus produce very limited photocurrent.^{5,17,18} The poor mobility combined with inherently slow water oxidation reactions often results in the high degree of electron and hole recombination either with the defect and trap states or within grain boundaries, which diminishes the efficiency of the photocatalytic reaction significantly. This is one of the biggest obstacles hindering the development of WO₃ as a practical photocatalyst.^{2,19} One possible technique of improving the efficiency of electron–hole pair separation in WO₃ is to dope WO₃ with other elements or compound (Ag, C, S, P, and TiO₂).^{1,2,19–22} In 2010, Sun *et al.* reported that Ag doped mesoporous WO₃, exhibited excellent photocatalytic decomposition of acetaldehyde under visible-light irradiation.¹ It has been reported that carbon doping enhances

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charges exchange rate and thus improves the photocatalytic activity of WO_3 .² Furthermore doping may also reduce the band gap of WO_3 and improves its photocatalytic efficiency, for instance the band gap of WO_3 nanowire array reduced from 2.8 to 2.2 eV after nitridation in a NH_3 atmosphere.¹⁹

Graphene (GR), with a flat monolayer of carbon atoms tightly packed into a two-dimensional honeycomb lattice, is a very promising candidate for high performance photocatalyst because of its high thermal conductivity,²³ excellent mobility of charge carriers ($20\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ at room temperature),²⁴ and a large specific surface area ($2630\text{ m}^2\text{ g}^{-1}$).²⁵ The combination of GR with a well photocatalytic semiconductor is expected to result in a high performance in photocatalytic activity. Recently, there are many reports concerning about incorporation of metal oxide (TiO_2 , $\text{Sr}_2\text{Ta}_2\text{O}_7$ and ZnO , etc.) on GR sheets to obtain composite photocatalysts.^{18,26,27} It has been shown that GR in the composites could act as electronic conductive channels to improve the electrochemical performance. From the point view of photo-conversion efficiency, the photocatalytic properties of semiconductor could be further enhanced if the recombination of the photoinduced electron-hole pairs can be effectively suppressed. Therefore, the composite consisted of nano WO_3 particles and two-dimensional GR sheets is a promising photocatalyst for oxygen production because GR can act as an electron transfer channel thus reducing the recombination of the photo-generated electron holes and leading to improved photo-conversion efficiency.^{3,5,18} Up to now, no investigation concerning about nano WO_3 particles on GR sheets for water splitting has been reported. To the best of our knowledge, only one paper concerning about the mixture of WO_3 powder and graphene oxide (GO) for *in situ* reduction under visible light was reported by Ng *et al.* But the WO_3 particle sizes were really large up to 100 nm and tended to aggregate during the physical mixing.²⁸ How to control the synthesis of crystalline WO_3 nanoparticles uniformly on the surface of the GR sheet is critically important. The crystallinity and the particle size of the photocatalyst are two important factors of affecting the photocatalytic activity.^{6,29–31}

Herein, we report for the first time the synthesis of a composite ($\text{WO}_3@\text{GR}$) consisting of WO_3 nanoparticles and GR sheets. The structures and morphologies of the composite were characterized by using a variety of measurements. The photocatalytic oxygen evolution properties of the $\text{WO}_3@\text{GR}$ composite was investigated by measuring the amount of oxygen evolved from water splitting and compared with those of pure GR, WO_3 and the mixture of WO_3 and GR (mixed- WO_3/GR).

Experimental

Preparation of GR

GR was obtained by chemical reduction of GO which was prepared from natural graphite (crystalline, 300 mesh, Alfa Aesar) by a modified Hummers method.³² The details of the preparation of the GO were described in our previous article.³³ In a typical reduction experiment, 0.5 g of GO powder was dispersed in 150 ml of deionized water and the mixture was sonicated for 1 h. Next, 18 ml of hydrazine (85%) was added under magnetic stirring, and the mixture was continuously stirred at 50 °C for 24 h. Finally, black GR powder was obtained by filtration and drying under vacuum at 60 °C.

Preparation of $\text{WO}_3@\text{GR}$

$\text{WO}_3@\text{GR}$ composite was synthesized by sonochemical reaction of phosphotungstic acid (AR, Sinopharm) in the presence of GO. The process of preparing $\text{WO}_3@\text{GR}$ composite is described as follows: 0.50 g of GO was added to 20 ml of H_2O and stirred for 12 h under magnetic vigorous stirring at ambient temperature. As the reaction progressed, GO was dissolved in the water, while the mixture gradually became pasty and the color turned into light brownish. At the same time, 1.2 g of phosphotungstic acid and 10 ml ethanol were mixed uniformly, and slowly added to the above GO mixture. Finally the suspension was sonicated at room temperature for 3 h using a high-intensity ultrasonic probe (Ti horn, 20 kHz, 100 W cm^{-2}). The resulting composite was recovered by centrifugation and rinsed with ethanol solvent and H_2O several times, then dried under vacuum at 60 °C to obtain amorphous WO_3 and GR composite ($\text{A-WO}_3@\text{GO}$). After calcination at 550 °C for 3 h under nitrogen, black crystallized $\text{WO}_3@\text{GR}$ composite was obtained.

For comparison, pure WO_3 powders were also prepared under the same condition without adding GO precursor in the process, and the mixed- WO_3/GR was prepared by mechanical mixing of pure WO_3 and GR, with the same composition as that in the $\text{WO}_3@\text{GR}$ composite.

Characterization

The synthesized samples were characterized by X-ray diffraction (XRD) using a RigakuD/max2550VL/PC system operated at 40 kV and 40 mA with Cu-K α radiation ($\lambda = 1.5406\text{ \AA}$), at a scan rate of 5° min^{-1} and a step size of 0.050° in 2θ . Nitrogen adsorption measurements at 77 K were performed using an ASAP2020 volumetric adsorption analyzer, after the samples had been outgassed for 8 h in the degas port of the adsorption apparatus. Field-emission scanning electron microscopy (FE-SEM) was performed on a JEOL JSM-6360LV field emission microscope at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and energy-dispersive X-ray measurements (EDX) were carried out on a JEOL 2010 microscope at 200 kV. TEM specimens were prepared by grinding the synthesized samples into powder with a mortar and pestle and the powder was dispersed in pure ethanol and picked up with holey carbon supporting films on copper grids. A Dilor LABRAM-1B microspectrometer with 633 nm laser excitation was used to record the Raman spectrum of the samples. Fourier transform-infrared measurements (FT-IR) were recorded on KBr pellets with a PE Paragon 1000 spectrophotometer. Thermal gravimetric analysis (TGA) was conducted on a PE TGA-7 instrument with a heating rate of $20\text{ }^\circ\text{C min}^{-1}$. Diffuse reflectance electronic spectra (DRS) were measured with a Perkin-Elmer 330 spectrophotometer equipped with a 60 mm Hitachi integrating sphere accessory.

Photocatalytic oxygen evolution experiments

Photocatalytic oxidation reactions were conducted at *ca.* 20 °C in a Lab Solar gas photocatalysis system with external light irradiation. The light source was a 300 W high pressure integrated type xenon lamp (PLS-SXE300/300UV, China). Before the photochemical reaction, 60 ml of ultra-pure water

was degassed by boiling it for 30 min and cooling to room temperature, and then added it to the reactor. Then 0.05 g of the photocatalyst (GR, WO₃@GR, WO₃ and Mixed-WO₃/GR) and 10 ml of 16.0 mmol l⁻¹ Fe₂(SO₄)₃ were added to the reactor in tandem under magnetic vigorous stirring to ensure the mixture suspense, using H₂SO₄ solution to adjust the pH of the mixture at 2. During the experiment, the reactor system was filled with flowing temperature-controlled cooling water. The amount of O₂ evolved was determined using gas chromatography (GC7890II, thermal conductivity detector, nitrogen carrier gas).

Results and discussions

The preparation process of the WO₃@GR composite is illustrated schematically in Scheme 1. After the dispersion of GO in the aqueous solution, phosphotungstic acid in ethanol was added under continuous stirring. Then the mixture was under ultrasonication for 3 h to fabricate WO₃ on the GO sheets (A-WO₃@GO). The crystallization of the amorphous WO₃ particles and the reduction of the GO to GR were achieved by the calcination of A-WO₃@GO at 550 °C for 3 h under nitrogen.

Wide-angle XRD patterns of the pure WO₃ powder, A-WO₃@GO and WO₃@GR are compared as shown in Fig. 1. The pure WO₃ sample is well crystallized in a single phase and all of the diffraction peaks can be indexed to monoclinic WO₃ (JCPDF 43-1035). As for the A-WO₃@GO composite, two broad peaks located at $2\theta = 26.4^\circ$, 10.6° were detected, corresponding to graphite carbon and GO with interlayer spacing of 0.34 nm and 1.02 nm, respectively.³⁴ A small peak at 19.5° is assigned to the residual intermediate of phosphotungstic acid (JCPDF 53-1015). No characteristic peaks of WO₃ were presented in the A-WO₃@GO composite before calcination. After calcination at 550 °C, the diffraction peaks which can be indexed to cubic WO₃ (JCPDF 20-1324) appeared, indicating the crystalline WO₃ formed on the GR sheets. Compared with that of A-WO₃@GO, the peak of carbon in WO₃@GR located at 26.4° became distinguished, suggesting the possible reduction of GO to GR occurred during the heat treatment process. This is consistent with the disappearance of the small peak at $2\theta = 10.6^\circ$ in the XRD pattern of WO₃@GR, attributed to the GO in A-WO₃@GO. The average particle size of the WO₃ in WO₃@GR can be estimated to be around 12 nm by applying the Scherrer formula.³⁵ This result suggests that the growth of nanocrystalline WO₃ on the GR sheets was very limited and controlled, which will be further confirmed by TEM.

Fig. 2 shows the TGA of GR and WO₃@GR in air by heating up from 40 to 900 °C. The largest weight loss occurs at temperatures from 530 to 690 °C for both GR and WO₃@GR, due to the destruction of the carbon skeleton (carbonyl/double bond). The weight loss of WO₃@GR was stabilized at about 40% at temperatures between 690 and 900 °C, which indicates that the amount of WO₃ loaded on the GR sheets was about 60 wt%. It is worth mentioning that a weight loss of 15 wt% was observed from 150 to 530 °C for GR, owing to the pyrolysis of the residual hydroxyl group on the surface of GR. Unlike the pure GR sample, only one large weight loss peak at 600 °C was observed for the WO₃@GR, illustrating that the WO₃ was most likely located on the surface of the supporting GR sheets and didn't form as separate material.

Fig. 3 shows a selected region of the Raman spectra of the pure WO₃, GR as well as WO₃@GR. As is expected, GR has two peaks at around 1350 and 1595 cm⁻¹.¹⁷ The G-band peak at around 1595 cm⁻¹ is characteristic of graphitic sheets, corresponding to a well defined sp² carbon-type structure.³⁶ Whereas, the D-band at around 1350 cm⁻¹ can be attributed to the presence of defects within the hexagonal graphitic structure.³⁷ Thus a smaller I_D/I_G peak intensity ratio of a Raman spectrum indicates lower defects and disorders of the graphitized structures. Similar peaks at D-band (1366 cm⁻¹) and G-band (1640 cm⁻¹) are also observed in the WO₃@GR composite. From the spectra in Fig. 3, we can see that the I_D/I_G ratio decreases from 1.16 for the GR sheets to 0.75 for the WO₃@GR composite. The higher I_D/I_G ratio of the GR is probably due to the formation of large number of multilayered GR (thin graphite) through GR restacking. The GR restacking in the WO₃@GR composite would be much reduced because the GR surfaces were coated with WO₃. Consequently the WO₃@GR composite has less lattice defects than the GR reduced from the GO. The smaller number of the defects will benefit to the photocatalytic activity of the WO₃@GR composites because these lattice defects normally act as recombination centers for the photo-generated electrons and holes. Moreover, Raman vibrations centered at 129, 276, 709, 801 cm⁻¹ characteristic of pure WO₃ were also detected in the sample of WO₃@GR composite. These bands are due to the stretching mode O–W–O. Compared with that of the pure WO₃ powder, the band at 709 cm⁻¹ attributed to W=O bonds was broadened and shifted to 678 cm⁻¹ for the WO₃ in the WO₃@GR composite, probably because the formation of C–O–W bonds makes the initial W=O bond weaker and a similar phenomena has been reported

Scheme 1 Synthetic procedure for the preparation of WO₃@GR composite.

Fig. 1 XRD of WO_3 , $\text{A-WO}_3\text{@GO}$ and $\text{WO}_3\text{@GR}$.

elsewhere.³⁸ This means that WO_3 was grafted onto the surface of GR layer *via* C–O–W bonds rather than physically adsorbed on the GR sheets. This kind of structure is desirable for charge transfer upon light excitation.³⁹ It is worth noting that a G-band up-shift from 1595 to 1604 cm^{-1} was observed for $\text{WO}_3\text{@GR}$ compared with GR. This G-band up-shift is generally an evidence of chemical doping of carbon materials. The trend was similar to previous studies with the p-type doping of the GR causing up-shift of the G-band.⁴⁰ The Raman G-band shift provides reliable evidence of charge transfer between the GR sheets and the WO_3 in the $\text{WO}_3\text{@GR}$ composite and suggests a dyadic bonding between the GR and WO_3 .

The interaction between the WO_3 and GR was also confirmed by FT-IR spectroscopy as shown in Fig. 4. C–O functionalities such as COOH (1724.8 cm^{-1}) and C–OH (1045.3 cm^{-1}) are clearly visible in the GO. The spectrum also shows a C=C peak at 1606.3 cm^{-1} corresponding to the remaining sp^2 character. As for $\text{A-WO}_3\text{@GO}$, the broad absorptions at low frequencies were ascribed to the vibration of W–O–W bond (below 1000 cm^{-1}) which was not observed in the spectrum of GO. It was found that the peak of the C–OH at 1045.3 cm^{-1} for GO shifted to a higher

Fig. 2 TGA curves of GR and $\text{WO}_3\text{@GR}$ (heating rate = 20 $^{\circ}\text{C min}^{-1}$ under air atmosphere).

Fig. 3 Raman spectra of pure WO_3 , GR and $\text{WO}_3\text{@GR}$.

wave number of 1079 cm^{-1} for $\text{A-WO}_3\text{@GO}$, which could be explained by the influence of the formation of C–O–W bond.

SEM images of GR, $\text{A-WO}_3\text{@GO}$ and $\text{WO}_3\text{@GR}$ are shown in Fig. 5. The pure GR has a layered structure with a very smooth surface (Fig. 5a and b), while the $\text{A-WO}_3\text{@GO}$ and $\text{WO}_3\text{@GR}$ composite shows a mass of wrinkles (Fig. 5c–f). The layered structure of the GR sheets in the $\text{WO}_3\text{@GR}$ composite exhibits nanoscale textures, indicative of a much rougher surface. In addition a large amount of WO_3 nanoparticles were observed clearly dispersion on both the GR surface and the interlayers without apparent agglomeration (Fig. 5e). Fig. 5f shows that the particle size is very uniform with tens nanometres in diameters, illustrating that ultrasonic sound irradiation is an effective method of fabricating WO_3 nanoparticles on the GR surface.

The structures and composition of the $\text{WO}_3\text{@GR}$ composite were further characterized by using TEM and EDX, and the results are shown in Fig. 6. From the low-resolution TEM (Fig. 6a), it can be seen there are plenty of wrinkles on the clean sheet owing to the two-dimensional nature of the matrix sheet. From the high resolution image, discrete and well defined WO_3 particles are uniformly scattered on the sheets with the particle size of around 12 nm (Fig. 6b). This observation is consistent with the wide angle XRD results presented in Fig. 1. As demonstrated in Fig. 6c, the measured lattice-fringe spacing of

Fig. 4 FT-IR spectra of GO, GR, $\text{A-WO}_3\text{@GO}$ and $\text{WO}_3\text{@GR}$.

Fig. 5 FE-SEM images of GR (a, b), A-WO₃@GO (c, d) and WO₃@GR (e, f) in different magnifications.

0.34 nm in the ribbons was detected corresponding to the (001) of the GR sheets; and the measured lattice fringe spacing of 0.36 nm in WO₃@GR composites corresponds to the (020) of cubic WO₃ (JCPDF 20-1324). Fig. 6 shows the EDX spectrum from the area shown in Fig. 6c. The TEM results provide the direct evidence of WO₃ nanoparticles on the surface of GR sheets.

N₂ adsorption/desorption isotherms of the samples WO₃ and WO₃@GR have been measured and are shown in Fig. 7. Both of the WO₃ and WO₃@GR samples show similar isotherm curves. The WO₃ sample has a specific surface area of 7.29 m²g⁻¹ according to the BET (Brunauer, Emmett and Teller) analysis and the specific surface area of the WO₃@GR samples is 20.72 m²g⁻¹. The increase of the surface area can be explained by the special structure of GR which has ordered two-dimensional honeycomb lattice and a large specific surface area (GR, 66.35 m²g⁻¹).

The light-absorbance properties of the pure WO₃, GR and WO₃@GR composite were studied with a UV-vis spectrophotometer and the obtained spectra are shown in Fig. 8. Both the GR and WO₃@GR show a similar spectrum shape with strong adsorption from UV to visible light region because their similar black appearance. At a wavelength above 500 nm the pure WO₃ has a much weaker absorption and different shape in comparison with those of the GR and WO₃@GR samples. As shown in Fig. 8, the light absorption intensity of WO₃@GR is stronger than that of GR due to the presence of 60 wt% WO₃ in the WO₃@GR composite. At the same time, the light absorption

Fig. 6 TEM images of WO₃@GR in different resolutions (a, b, and c) and EDX images.

Fig. 7 N_2 adsorption/desorption isotherms of samples WO_3 and $WO_3@GR$.

intensity of $WO_3@GR$ is also much stronger than that of WO_3 in visible light range resulting from the existence of 40 wt% GR in the $WO_3@GR$ composite. DRS demonstrate the synergistic effect of GR and WO_3 contributed to an improved light harvesting property. This is expected to result in an improved photocatalytic activity over the complete spectral range.

The photocatalytic activities of the $WO_3@GR$, pure GR, pure WO_3 and mixed- WO_3/GR in terms of O_2 generation from water were measured using a Lab Solar gas photocatalysis system with external light irradiation and the results are shown in Fig. 9. In order to remove the gas dissolved in water, before the photochemical reaction, ultra-pure water was boiled for 30 min and cooled to room temperature. Fig. 9 shows the amount of evolved O_2 of photocatalyst (GR, WO_3 , mixed- WO_3/GR and $WO_3@GR$) by solar light from an aqueous solution containing the Fe^{3+} ion as an electron acceptor. The amount of evolved O_2 from the aqueous solution after 9 h for the $WO_3@GR$ was *ca.* $388 \mu\text{mol L}^{-1}$, which is more than 1.8 times and twice as much as

Fig. 8 Diffuse reflectance electronic spectra of pure WO_3 , GR and $WO_3@GR$.

Fig. 9 Time course of O_2 evolution from the solution with suspended photocatalyst (WO_3 , GR, mixed- WO_3/GR and $WO_3@GR$) under xenon lamp irradiation.

that of the mixed- WO_3/GR (*ca.* $214 \mu\text{mol L}^{-1}$) and WO_3 (*ca.* $186 \mu\text{mol L}^{-1}$), respectively.

In our photocatalytic oxygen evolution experiments, illumination photons create electron-hole pairs in the WO_3 at the solid-solution interface (eqn 1). These electron-hole pairs separate and reach to the photocatalyst surface by diffusion. WO_3 is photocatalyst with weak reducing power owing to their positive conduction band position ($> 0 \text{ eV vs. NHE at pH} = 0$), which prohibits the electron transfer to reduce H_2O to H_2 .⁴¹ Therefore, only holes reaction with water to produce O_2 can occur spontaneously by using these photocatalyst (eqn 2). However, electron-hole pairs are very easily to recombine either with defect and trap states or within grain boundaries quickly, which diminishes the efficiency of the photocatalytic reaction significantly. Generally, a scavenger is used to reduce the recombination of electron-hole pairs in order to enhance charge transport rate and improve photocatalytic activity. Here, $Fe_2(SO_4)_3$ was used as the scavenger. The Fe^{3+} ion would react with photo-induced electrons as an electron acceptor to reduce the recombination of electron-hole pairs (eqn 3).

The total equation for the photocatalytic O_2 production may be summarized in the following:

It should be noted that the amount of evolved O_2 from mixed- WO_3/GR (60 wt% WO_3 and 40 wt% GR) was measured about $214 \mu\text{mol L}^{-1}$, which was much lower than that from the obtained $WO_3@GR$ composite ($388 \mu\text{mol L}^{-1}$). The difference could be mainly due to the structure of the $WO_3@GR$ composite. The chemical bonds (C–O–W *etc.*) between WO_3

and GR sheets suggested by the shift of Raman peak and FT-IR (Fig. 3 and Fig. 4), which do not only enhance the optical adsorption by sensitizing the WO_3 in visible light, but also significantly enhance charge separation efficiency and carrier transfer rate. A similar phenomenon has also been observed by Zhao *et al.* in the carbon@ TiO_2 with a “dyade” structure.⁵ The enhanced visible-light absorption was explained as the surface nanometre carbon materials which can show collective polarization modes and sensitize semiconductors.

GR has a charge-carrier mobility of $20\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, so it is very possible that the incorporation of GR might enhance the charge separation efficiency and suppress the charge recombination as suggested by Scheme 2. Under visible light illumination, electrons in the valence band (VB) acquire enough energy and jump into the conduction band (CB) of WO_3 , leaving positive charged holes in the VB. GR with a two-dimensional conjugated π - π graphitic carbon network and superior electrical conductivity could efficiently transfer the photo-generated electrons away from the WO_3 . Finally, the electrons were quickly scavenged by the electron acceptor of Fe^{3+} in the solution,⁴² while the holes in the VB reacted with H_2O to produce O_2 . Thus GR served as an acceptor of the CB electrons of the WO_3 and effectively suppressed the charge recombination in WO_3 @GR sample, leaving more positive charged holes on the WO_3 surface and thus promoting the production of oxygen.^{43,44}

Zhang *et al.* reported that the photocatalytic activity would decrease distinctly with the content of GR exceeding 5 wt% in GR/ TiO_2 composite by introducing electron-hole recombination centers into the composite.¹⁸ Surprisingly, in our case the percentage of GR in WO_3 @GR nanocomposite reached as high as 40 wt%, it still showed an enhanced photocatalytic activity (Fig. 9). It could be explained by the bonds between the GR and WO_3 in the WO_3 @GR composite. Carboxylic species of the GO interacting with the precursor of the WO_3 particles enable the dispersion and adhesion of particles onto the GO as suggested by Raman and FT-IR measurements. The close contact and bonds would enable easy charge transfer between the WO_3 particles and GR sheets. As evidenced by the I_D/I_G ratios in the Raman spectra, the GR in WO_3 @GR composite contains less lattice defects than the stand alone GR so that the electron-hole recombination rate would be much lower for the WO_3 @GR

composite. In Zhang's case, there is no chemical bond between the mixed GR and powder TiO_2 so that the interface boundaries become the recombination centers for electrons and holes.

Furthermore, the crystallinity and the particle size of the photocatalyst are also important factors to the photocatalytic activity.^{6,30,31} The higher the crystalline quality of the WO_3 is, the less amount of defects it has. Defects can operate as recombination centers between the CB electrons and VB holes and reduce the photocatalytic activity. The smaller the particle size is, the shorter time need for electron-hole pairs moving from inner to surface, which will decrease the electron-hole pairs recombination and enhance the photocatalytic activity. Clearly the photocatalytic activity of the WO_3 @GR composites is much better than both the pure WO_3 and the mixed- WO_3 /GR due to the synergistic effects from WO_3 and GR in the photocatalytic process.

The same process has been extended to the fabrication of Bi_2WO_6 on the surface of GR sheets (GR- Bi_2WO_6 -T). As is expected, the combination of functionality of Bi_2WO_6 with the unique properties of GR results in an improved performance in O_2 production from water splitting (Fig. 10). Therefore, this methodology opens up a new way of obtaining photoactive GR-semiconductor composites for photodissociating water under visible light.

Conclusions

WO_3 @GR composite, a visible light photocatalyst, was successfully synthesized using a sonochemical method in a short time. SEM and TEM provided direct evidence that a fine and uniform distribution of WO_3 nanoparticles formed on the surface of GR sheets. The average particle size of the WO_3 was controlled at around 12 nm on the GR sheets without using any surfactant. When used as photocatalyst for water splitting, the amount of evolved O_2 from WO_3 @GR with 40 wt% GR inside is much higher than that of pure WO_3 and mixed- WO_3 /GR, 1.8 times and 2 times as much as that from mixed- WO_3 /GR (*ca.* $214\text{ }\mu\text{mol L}^{-1}$) and pure WO_3 (*ca.* $186\text{ }\mu\text{mol L}^{-1}$), respectively. The improved performance is due to the synergistic effects of chemically bonded WO_3 and GR. The sensitization of WO_3 by GR enhanced the

Scheme 2 The procedure of photocatalytic oxidation for the WO_3 @GR composite.

Fig. 10 Time course of O_2 evolution from the solution with suspended photocatalyst (Bi_2WO_6 , GR and GR- Bi_2WO_6 -T) under xenon lamp irradiation.

visible light absorption property of WO₃@GR. The chemical bonding between WO₃ and GR reduced the recombination of the photo-generated electron–hole pairs, leading to improved photo-conversion efficiency. This simple strategy opens up a new way to design more optimized systems for photodissociating water under visible light.

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