Reduced Graphene Oxide Three-Dimensionally Wrapped WO₃ Hierarchical Nanostructures as High-Performance Solar Photocatalytic Materials

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Abstract

A unique reduced graphene oxide (RGO) three-dimensionally wrapped WO₃ (WO₃@RGO) composite was synthesized via a facile one-step hydrothermal method. In this composite, the building blocks of the WO₃ hierarchical structure, the nanobelts, were intimately wrapped by a layer of RGO. Due to the synergistic effect of the hierarchical structure of WO₃ and intimately wrapped RGO on the surface of the nanobelts, the WO₃@RGO showed much higher photocatalytic performance in degrading rhodamine B and phenol under simulated solar light irradiation than the bare WO₃ and other composites in which only the mainframe of WO₃ was wrapped by RGO. Moreover, the photocatalytic activity was significantly influenced by the loading amount of RGO. The optimal performance was found in the 1.2% WO₃@RGO, which was about 2.50 times that of the bare WO₃. Conclusively, using graphene to wrap the building blocks rather than only the mainframe

of semiconductors is anticipated to be a promising method to achieve high-performance photocatalysts for solar energy conversion.

Key Words

WO₃ hierarchical nanostructures, RGO three-dimensionally wrapping, solar light photocatalysis, charge transfer

1. Introduction

The serious environment pollution and energy crisis due to the extensive utilization of fossil fuels are considered as the two major challenges in the 21st century. Among various technologies available today, heterogeneous photocatalysis based on semiconductors making use of renewable solar energy has been regarded as one of the most promising strategies for solving both the environmental and energy issues, and has thus received much attention during recent decades.[1,2] However, the low quantum efficiency, high recombination rate of the photoproducted electron-hole pairs, poor absorption capacity, and deactivation of the semiconductor photocatalyst limit the practical application of semiconductor-based photocatalytic technique.[3] Fortunately, due to its unique features, graphene-based semiconductor photocatalyst was thought to be one of the most promising candidates to deal with these concerns. In the past few years, many encouraging achievements have been made in the research of graphene-based semiconductor photocatalysts.[3-5] Graphene is a two-dimensional (2D) material composed of sp²-bonded carbon atoms that are linked in hexagonal shapes, with each carbon atom covalently bonded to three other carbon atoms.[6] Graphene has a large theoretical specific surface area, superior mobility of charge carriers, and high

thermal/chemical stability.[7] With these superior features, the light absorption can be enhanced and the number of active adsorption sites and reaction centers can be increased by introducing graphene. More significantly, as a conductive channel, good acceptor and reservoir of the photogenerated electrons, graphene could greatly promote the separation of photoinduced charges, improve the interfacial charge transfer, and prolong the lifetime of photogenerated electron-hole pairs, thus remarkably boosting the photoactivity of graphene/semiconductor nanocomposites.[1,3,8]

There are many factors that affect the performance of graphene-based semiconductor photocatalysts. One major factor is the interfacial interaction between the graphene and the semiconductor, which is considered essential for the effective transfer of photoinduced electrons. [9,10] The decreased electron-hole recombination and extended charge-carrier lifetime resulting from the electron transfer is proposed as the key factor for improving the photocatalytic performance of graphene-based semiconductor photocatalysts.[11] Typically, the increased tightness and contact area of the interfacial coupling between the graphene and semiconductor are favorable for an efficient electron transfer.[10] Up to date, the most widely reported configuration of graphene-based semiconductor photocatalyst is semiconductor nanoparticles being homogeneously distributed on the graphene sheets.[12-21] However, the contact area between the 2D graphene sheets and the semiconductor nanoparticles in this configuration is small, which limits the electron transfer from the semiconductor nanoparticles to the graphene.[6,22,23] To solve this problem, the semiconductor nanoparticles or nanorods wrapped or coated by graphene were developed and the photoactivity were greatly improved. [6,7,24-28] Kim *et al.*[28] found that the small piece graphene coated TiO₂ showed a better performance than the large piece graphene coated TiO₂, due to TiO₂ being completely coated and in close contact with graphene. Feng *et al.*[7] successfully prepared graphene encapsulated

mesoporous hollow TiO₂ nanospheres via a multistep method and they found that the composite exhibited an excellent photocatalytic performance for rhodamine B (RhB) degradation due to the synergistic effect of the mesoporous feature of TiO₂ and well enwrapped graphene shell. The graphene-ZnO quasi-shell-core composite was synthesized by Chen *et al.*[6] using a wet chemical method and the electron migration ability of this composite was significantly enhanced because the surface of the ZnO was coated by graphene.[6] These all indicate that the strategy of closely wrapping or coating the semiconductors by graphene is beneficial for the electron transfer. However, it is still a challenge to develop effective methods to achieve a more intimate contact between the graphene and semiconductor.

In addition to strengthen the interfacial coupling, another effective method to optimize the photocatalytic activities is improving the quality of individual components.[29,30] Semiconductor nanoparticles,[10,31] nanospheres,[27] nanorods,[32,33] and nanowires[34,35] have been used to construct the graphene-based semiconductor photocatalyst. Among them, one-dimensional (1D) semiconductor nanostructures received the most attention, which can offer a direct pathway for the photogenerated charges.[36] Besides, the three-dimensional (3D) hierarchical structures assembled with 1D nanosized building blocks also have attracted many interests because it can provide more active sites with considerable large specific surface area. Both the light utilization efficiency and structure stability can be achieved in the hierarchical photocatalysts.[37,38] Therefore, the construction of a composite with graphene and 1D nanostructure or 3D hierarchical structure assembled with 1D nanosized building blocks is desirable.

Herein, a unique reduced graphene oxide (RGO) three dimensionally wrapped WO₃ composite (WO₃@RGO) was synthesized via a facile one-step hydrothermal method. In the WO₃@RGO, the

1D building blocks of the hierarchical WO_3 were homogeneously and closely wrapped by a layer of RGO. In order to highlight the superior photocatalytic property of this composite, the bare WO_3 and other composites, in which only the mainframe of the WO_3 hierarchical structure was wrapped, were also prepared. Our work demonstrates a facile strategy to realize a strong synergistic effect between the 2D graphene sheet and 3D hierarchical structured semiconductor.

2. Experimental

2.1. Materials preparation.

All chemicals were purchased from the Sinopharm Chemical Reagent Co., Ltd and were of analytical reagent grade and used without further purification. All the aqueous solutions were prepared using deionized water.

2.1.1. One-step synthesis of the WO_3 @RGO composites.

The WO_3 @RGO composites were synthesized through a one-step hydrothermal reaction. In a typical process, the 1 mg mL^{-1} homogeneous graphene oxide (GO) suspension was obtained by ultrasonication and diluted into 168 mL GO suspension with deionized water. Then 1.25 g tungstic acid was added into 25 mL H_2O_2 , stirred at 90°C for 1.5 h before converting into a transparent sol. The resulting clear sol was diluted to 60 mL using deionized water, and then 42 mL of the as-prepared solution and 14 mL 3 M HCl were added to the 168 mL GO suspension. After stirring for another 20 min, 30 mL of the precursor solution was transferred into a 50 mL Teflon-lined autoclave followed by adding 40 μL formamide and 0.144 g urea. Finally, the autoclave was sealed and maintained at 180°C for 12 h. The as-synthesized precipitate was washed with deionized water for three times and alcohol for two times by centrifugation, and then dried in vacuum at 80°C for 3 h.

These samples were labeled as x WO₃@RGO, where x stands for the weight percentage of GO to tungstic acid in the precursor solution, which varies from 0 to 4.8%, depending on the ratio of the starting materials during the synthesis.

2.1.2. Synthesis of WO₃/GO, HyWO₃/GO and WO₃/RGO composites.

Bare WO₃ was also obtained through a similar procedure as the WO₃@RGO composites but without adding GO. The WO₃/GO composite was synthesized by adding bare WO₃ powder into the GO suspension (x=1.2%) under stirring. The HyWO₃/GO composite was obtained by a hydrothermal reaction in which the above WO₃-GO suspension (30 mL) was transferred into a 50 mL Teflon-lined autoclave and sealed and maintained at 180 °C for 12 h. Meanwhile, the WO₃/RGO composite was prepared by adding ascorbic acid (LAA) into the above WO₃-GO suspension and stirring for 48 h in 60 °C water bath. The as-synthesized precipitates were washed with deionized water for three times and alcohol for two times by centrifugation, and then dried in vacuum at 80 °C for 3 h. The WO₃/GO, HyWO₃/GO and WO₃/RGO were prepared by adding the same amount of GO (x=1.2%).

2.2. Measurements of photocatalytic property and photoelectrochemical property.

Photocatalytic properties of the samples were evaluated by measuring the concentration of RhB and phenol in the aqueous solution after equilibration in the dark and irradiation with simulated solar light achieved from a 300 W Xenon lamp. Typically, 20 mg sample was dispersed in 40 mL RhB aqueous solution (20 mg L⁻¹). Before the sample was exposed to light irradiation, the suspension was stirred over night to ensure the equilibrium of dye adsorption on the surface of the sample. About 3 mL of the solution was taken every 20 min during the photodegradation process, and the powder sample was separated from the solution via centrifugation. Then the RhB concentration was measured by UV–Vis spectroscopy via tracing the absorption. The photodegradation of phenol (10

mg/L) was conducted in a similar procedure to RhB. The concentration of phenol was determined by the chromatographic experiments performed using an HPLC-UV/Vis system with an ultraviolet absorbance detector (K 2501) operated at 270 nm and a Venusil XBP-C₁₈ (Agela Technologies Inc.) column.

The photocurrents were measured on an electrochemical workstation (CHI-660E, China) and carried out in a conventional three-electrode system with a working electrode, a platinum wire as counter electrode and a standard calomel electrode (SCE) as reference electrode. 0.1 M Na₂SO₄ was used as the electrolyte solution. The photoelectric responses of the photocatalysts were measured at 0.0 V (vs. SCE). The working electrodes were prepared by a dip-coating method: 10 mg photocatalyst was suspended in 1 mL 1-methyl-2-pyrrolidinone (NMP) to make a slurry, and the slurry was then dip-coated onto a 2×3 cm fluorine-tin oxide (FTO) glass. The as-prepared electrodes were dried at 80 °C for 10 h in air.

2.3. Characterization of materials.

Crystallographic structures of the as-prepared materials were characterized by powder X-ray diffraction (XRD, Cu K α , Rigaku D/max-V2500, Japan). Morphologies and microstructures were studied using scanning electron microscopy (SEM, Zeiss, Germany) and transmission electron microscopy (TEM, JEM-2100F, JEM-2100 and HT7700, Japan). UV/Vis absorption spectra were recorded with UV-Vis spectrophotometer (U-3010, Hitachi, Japan). The X-ray photoelectron spectroscopy (XPS) measurements were determined on an Escalab 250Xi instrument (Thermo Fisher Scientific, USA). The surface areas of the samples were measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption-desorption isotherms at 77 K with an American Contador QuadraSorb SI-MP instrument. The Raman spectra were recorded by high-resolution Raman

spectroscopy (HR800, Horiba Jobin Yvon, France). Fourier transform infrared (FT-IR) spectra were carried out using Bruker V70 spectrometer in the frequency of 400-4000 cm^{-1} . Electron spin resonance spectroscopy (ESR) measurements were performed at room temperature with a JEOL FA200 ESR spectrometer under simulated solar light. Total organic carbon analyzer (TOC-VCPH, Shimadzu) was employed for photodegradation degree analysis.

3. Results and discussions

3.1 Structure and morphology.

The crystalline structures of the 1.2% WO_3 @RGO, bare WO_3 and GO were examined by XRD as shown in Fig. 1. For GO, the peak at about 10.8° is attributed to the (002) reflection of the stacked GO sheets, corresponding to an interlayer spacing of 0.84 nm. The increment in the interlayer distance compared with the pristine graphite (0.34 nm) is due to the introduction of oxygen-containing functional groups generated during the oxidation process and interlamellar water molecules trapped between the hydrophilic GO sheets.[39] As for the bare WO_3 , all of its diffraction peaks can be indexed to the hexagonal WO_3 (JCPDS 85-2460). The XRD pattern of the 1.2% WO_3 @RGO is similar to that of bare WO_3 but without the peak assigned to the stacked GO sheets, which is due to successful conversion of GO to RGO in the final composite and the low content and relatively low diffraction intensity of RGO. In addition, the x WO_3 @RGO, WO_3 /GO, HyWO_3 /GO and WO_3 /RGO all share similar XRD pattern to that of the bare WO_3 , and all samples possess high crystallinity, suggesting that the adding of GO does not change the crystal structure of WO_3 .

The XPS were utilized to investigate the chemical states of GO and the 1.2% WO_3 @RGO. The XPS spectrum of C 1s and the corresponding fitting curves for the GO are shown in Fig. 2a. The

peaks with a binding energy centered at 284.4, 287.0 and 288.7 eV can be attributed to the C-C, C-O and C=O bonds, respectively.[40] While in the 1.2% WO₃@RGO, the major peak of the C 1s spectrum has shifted to 284.7 eV, and the peaks corresponding to the C-O (286.4 eV) and C=O (288.8 eV) bonds are significantly weakened, suggesting the effective reduction of the GO after the hydrothermal reaction (Fig. 2b). Meanwhile, two peaks at 36.0 eV and 38.2 eV can be identified in the XPS spectrum of W 4f of the 1.2% WO₃@RGO (Fig. 2c), corresponding to W 4f_{7/2} and W 4f_{5/2} of the W⁶⁺ formal oxidation state, respectively. The O 1s of the 1.2% WO₃@RGO displays a relatively wide, asymmetric peak, with the highest point at 530.7 eV, which could be assigned to the oxygen bonded with W atoms (Fig. 2d). Another peak at higher photoelectron energy of 531.8 eV may be attributed to the residual water, O-C and C=O bonds originating from the residual oxygen-containing groups.[41]

Morphological features of the bare WO₃, 1.2% WO₃@RGO, WO₃/GO, HyWO₃/GO, and WO₃/RGO were examined by SEM. The bare WO₃ appears as microspheres assembled with nanowires, as shown in Fig. 3a. The 1.2% WO₃@RGO (Fig. 3b) contains two different kinds of morphology: either contains numerous small nanoflowers (Fig. 3c) or has some self-assembled microspheres with nanowires which are similar to the bare WO₃ (Fig. 3d). Fig. 3e shows the morphology of the WO₃/GO, in which the mainframe of the microspheres is wrapped by a thin layer of GO sheets. The wrapped GO sheets would disappear when the WO₃/GO suspension experienced a hydrothermal process (HyWO₃/GO). The HyWO₃/GO shows similar morphology to that of 1.2% WO₃@RGO, which contains some microspheres and smaller nanoflowers (Fig. 3f-3g). When the ascorbic acid (LAA) was added in the WO₃/GO suspension, the GO sheets on the surface of microspheres were reduced. As a result, the mainframe of WO₃ microspheres is wrapped by the RGO

(WO₃/RGO), as shown in Fig. 3h.

Further information on the microstructures of these samples was obtained by TEM and high resolution transmission electron microscopy (HRTEM). The exfoliated GO was used as the precursor to fabricate graphene/WO₃ composites. A crumpled structure with several stacking layers is observed from the TEM image of the GO in Fig. 4a. The 1.2% WO₃@RGO containing big microspheres and small nanoflowers were also shown in Fig. 4c. The nanowires in the microspheres or nanoflowers have a width about 10 nm and a length of several hundred nanometers, as shown in Fig. 4b, 4d, 4f and 4h. Moreover, the images also show that the nanowires are ultrathin, suggesting that the microspheres or nanoflowers in both bare WO₃ and 1.2% WO₃@RGO are assembled with nanobelts rather than nanowires. The nanoflowers in the 1.2% WO₃@RGO with a diameter of 200 nm are surrounded by agglomerated RGO forming a RGO-WO₃ nanoflowers network, as shown in Fig. 4e. Because the agglomerated RGO-WO₃ nanoflowers network is existed in both 1.2% WO₃@RGO and HyWO₃/GO, it is inferred that the RGO-WO₃ nanoflowers network may stem from the free-standing nanobelts which did not form the microsphere, were collected by the agglomerated RGO and then assembled into the nanoflowers during the hydrothermal reaction. The bare WO₃, HyWO₃/GO, and 1.2% WO₃@RGO all show the same lattice fringes of 0.382 and 0.315 nm corresponding to (002) and (200) planes of the hexagonal WO₃, indicating that the lattice structure of WO₃ is not changed after introducing RGO, as shown in Fig. 4g-4i. The edge and core region of the nanobelt show the same lattice structure both in the bare WO₃ and HyWO₃/GO (Fig. 4h and 4i). While the lattice structure in the outer boundary of the nanobelts in the 1.2% WO₃@RGO is distinct from that in the core region (Fig. 4f-4g), suggesting that the surface of the nanobelts in the 1.2% WO₃@RGO are coated with a thin layer RGO (about 1-3 nm). It can be further confirmed by bright-field scanning

transmission electron microscopy (BF-STEM) and electron energy loss spectroscopy (EELS) chemical mapping results of the 1.2% WO₃@RGO, as shown in Fig. S1. The distribution of carbon is consistent with that of oxygen and tungsten over the nanobelt surface, suggesting a homogeneous wrapping of RGO around the WO₃ nanobelt. The process of RGO closely wrapping the WO₃ nanobelts may occur through the electrostatic interaction between the positively charged amine-modified tungsten oxides, which originates from the urea and formamide added in the hydrothermal precursor solution, and the negatively charged GO nanosheets.[42]

From the above analysis of SEM and TEM images, it can be concluded that there exist four contact types between RGO or GO and WO₃ as shown in Scheme 1: I) the mainframe of WO₃ microspheres is wrapped by the thin GO via stirring the GO-WO₃ suspension (WO₃/GO); II) the mainframe of WO₃ microspheres is wrapped by the thin RGO through a mild reduction of WO₃/GO (WO₃/RGO); III) the WO₃ nanoflowers are surrounded by the agglomerated RGO forming RGO-nanoflowers network, which exists in both HyWO₃/GO and 1.2% WO₃@RGO; IV) the WO₃ nanobelts are closely wrapped by the thin RGO sheets, and only the microspheres and nanoflowers in the WO₃@RGO are assembled with this kind of nanobelts. When the mainframe of WO₃ microspheres or the WO₃ nanoflowers is wrapped or surrounded by RGO or GO, there may exist some gaps between them as shown in Scheme 1d(I), suggesting that the RGO or GO and WO₃ are not closely contacted in type I-III. However, type IV can offer much closer contact between RGO and WO₃ (see Scheme 1d(II)).

The closer contact in the 1.2% WO₃@RGO can be further confirmed by the Raman spectra as shown in Fig. 5. As for the GO, there are two peaks centered at 1332 and 1595 cm⁻¹, assigned to sp³ (D band) and sp² (G band) hybridized carbon atoms, respectively. All composites present similar D and G band structures, which belong to the characteristic peaks of graphene. It is noticeable that the

position of G band are shifted from 1595 to 1610 cm^{-1} and the broader D bands shifted from 1332 to 1341 cm^{-1} are observed in the 1.2% $\text{WO}_3\text{@RGO}$, suggesting a chemical interaction between RGO and WO_3 . While the WO_3/GO , HyWO_3/GO and WO_3/RGO composites show almost the same positions of D band and G band as GO, which provides reliable evidence of the superior interaction between RGO and WO_3 in the 1.2% $\text{WO}_3\text{@RGO}$. [43] Meanwhile, the UV-Vis spectra in Fig. S2 show that the light absorption intensity is enhanced after introducing GO or RGO. Especially, the 1.2% $\text{WO}_3\text{@RGO}$ shows the highest light absorption among the four composites. It suggests that the superior contact between RGO and WO_3 may be beneficial for the light absorption. However, these four composites show similar FT-IR spectra to that of the bare WO_3 . Moreover, the peaks belonging to GO such as 1732 and 1037 cm^{-1} , which correspond to the C=O and C-O-C groups, [11] are invisible in these four composites as shown in Fig. S3. This change may be attributed to the reduction of GO or the relatively low (1.2%) graphene loading. [11,44]

Except the contact type, the photocatalytic performance may also be influenced by the amount of RGO in the graphene/semiconductor composite. Therefore, it is necessary to further study the $\text{WO}_3\text{@RGO}$ composites with different amount of GO. The SEM images of the x $\text{WO}_3\text{@RGO}$ composites are presented in Fig. 6. The 0.6% $\text{WO}_3\text{@RGO}$ appears as smooth microspheres (Fig. 6c) which results from the changed ratio of formamide and urea caused by GO during the hydrothermal reaction (the detailed explanation in Supporting information, Fig. S2), thus leading to a decreased specific surface area (Table S1). Both the 1.8% and 2.4% $\text{WO}_3\text{@RGO}$ composites (Fig. 6b and 6c) show similar morphology as the 1.2% $\text{WO}_3\text{@RGO}$ (Fig. 3b), i.e. they all display the morphology of the big microspheres and RGO- WO_3 nanoflowers network. Because the nanoflowers origin from the free-standing nanobelts which are also contained in the bare WO_3 and the size of nanoflowers is

small, the specific surface areas of the 1.2-2.4% $\text{WO}_3\text{@RGO}$ composites only change a little compared with that of bare WO_3 (see Table S1). However, too much GO in the solution would result in bigger nanoflowers and the WO_3 nanoflower or nanobelts wrapped by thick RGO layers as shown in Fig. 6d and Fig. S5, leading to the obvious decreased specific surface area of the 4.8% $\text{WO}_3\text{@RGO}$ (Table S1). Meanwhile, the Raman spectra suggest an increasing intensity ratios of the D band to the G band with the increasing amount of GO, perhaps due to the agglomeration and incompletely reduction of GO,[35] as shown in Fig. S6a. Moreover, the light absorption intensity of $\text{WO}_3\text{@RGO}$ composites in both UV and visible light regions is also enhanced with the increase of the loading amount of RGO (Fig. S6b).

3.2 Photocatalytic performance.

The photocatalytic activities of the as-prepared samples for the degradation of RhB in the aqueous solution were measured under simulated solar light irradiation, as shown in Fig. 7. The degradation processes are fitted to pseudo-first-order kinetics, and the value of the rate constants κ are equal to the corresponding slope of the fitting lines. The average values from three parallel tests, are presented in Fig. 7c and 7f. The contact types between RGO or GO and WO_3 have a remarkable influence on the photocatalytic performance, as shown in Fig. 7a-7c. When the mainframe of WO_3 microsphere is wrapped by GO (WO_3/GO), the photocatalytic performance is slightly improved compared with that of bare WO_3 . While the WO_3/RGO has a better performance than that of the WO_3/GO due to the extremely high conductivity of RGO, which facilitates the rapid charge carriers migration across its 2D plane to reactive sites.[23] The HyWO_3/GO with extra RGO-WO_3 nanoflowers network shows slightly higher photocatalytic activity than that of bare WO_3 , suggesting

that the aggregated RGO surrounding the WO_3 nanoflower could improve the photoactivity but with limited effect. However, the 1.2% WO_3 @RGO shows a significantly enhanced performance compared with that of HyWO_3/GO , indicating that the RGO closely wrapping the WO_3 nanobelts could effectively improve the photocatalytic activity. Furthermore, the TOC removal rates of different wrapping samples were also investigated to study the photodegradation degree of RhB, as shown in Fig. S7. The TOC removal rates of the bare WO_3 , WO_3/GO , HyWO_3/GO , WO_3/RGO , and 1.2% WO_3 @RGO are 21%, 33%, 25%, 48% and 67%, respectively, corresponding to the variation of photocatalytic performance (Fig. 7a-7c). The 1.2% WO_3 @RGO has the highest removal rate, further confirming its excellent photocatalytic performance. Meanwhile, the adsorption experiments of different wrapping samples were also conducted. The 1.2% WO_3 @RGO shows only slightly higher adsorption of RhB than the bare WO_3 , while HyWO_3/GO , WO_3/GO and WO_3/RGO have an obvious enhanced adsorption, as shown in Fig. S8a, indicating that the enhanced photocatalytic activity of 1.2% WO_3 @RGO is mainly attributed to the superior contact type rather than the enhanced adsorption. The increased adsorption of WO_3/GO and WO_3/RGO may partly contribute to their improved photocatalytic performances. Fig. S9 shows that the photocatalytic performance of the 1.2% WO_3 @RGO only has a small decline after four cycles, showing good stability during the photodegradation tests. The XRD and XPS were also measured to study the structure stability of the 1.2% WO_3 @RGO after photodegradation, as shown in Fig. S10. The XRD pattern (Fig. S10a) maintains the same with that of the sample before photocatalysis test. In the XPS, the peaks corresponding to C1s, W4f and O1s (Fig. S10b-S10d) only slightly shift compared with the original one, also indicating good stability.

To eliminate the effect of dye self-sensitization on the photocatalytic activity, colorless phenol

was further adopted as the pollutant target. Fig. 8 shows the photocatalytic activities of the bare WO_3 , HyWO_3/GO , WO_3/RGO and 1.2% $\text{WO}_3@\text{RGO}$ on the photodegradation of phenol under simulated solar light (the activity of WO_3/GO was not measured because the GO in the WO_3/GO composite was apt to separate out in the phenol solution). The variation of photocatalytic performance of these four samples is similar to that on photodegradation of RhB (Fig. 7a-7c). The 1.2% $\text{WO}_3@\text{RGO}$ has the highest degradation rate among all the wrapping samples which could degrade 30% phenol (10 mg/L) within 240 min, demonstrating a high photocatalytic performance. To prepare the graphene-based composites, one of the most common approaches reported in the literature was distributing semiconductor particles or 1D nanostructures (referring to “hard” integration) on the surface of graphene nanosheets.[22] This strategy do not make full use of the structural advantage of 2D RGO,[45] which is very similar with the case when the mainframe of WO_3 microspheres or nanoflowers are wrapped or surrounded by RGO or GO (Type I-III in Scheme 1). However, the building blocks of the WO_3 microspheres, the nanobelts, are completely and tightly wrapped by RGO in the $\text{WO}_3@\text{RGO}$ (Type IV in Scheme 1). This configuration could offer much closer contact between the RGO and WO_3 , greatly prolonging the lifetime and improving the electron transfer, and thus leading to a low recombination of electron and hole.

Many researches showed that the photocatalytic performance of the graphene/semiconductor composite strongly depended on the amount of graphene added.[6, 24, 41] In order to achieve the optimal photocatalytic activity, the amount of RGO was adjusted in the $\text{WO}_3@\text{RGO}$ composites. The adsorption and the photocatalytic activities of $\text{WO}_3@\text{RGO}$ composites were measured and shown in Fig. S8b and Fig. 7d-7f. Fig. S8b shows that all the composites achieve adsorption equilibrium after stirring for 3 h in the dark, and as the amount of RGO increases, the final adsorption percentage

increases first, reaches its top value in the 1.2% WO₃@RGO and then decreases. Moreover, the photocatalytic performances of the WO₃@RGO composites (Fig. 7f) show similar trend to that of adsorption rate. These all suggest the close relationship among the adsorption rate, photocatalytic performance and the amount of RGO loading. All the WO₃@RGO composites except 0.6% WO₃@RGO perform better than the bare WO₃, as shown in Fig. 7d-7f. The photocatalytic performance of the 0.6% WO₃@RGO is lower than that of bare WO₃ due to its obviously decreased specific surface area and the declined adsorption. The optimal photocatalytic performance is found in the 1.2% WO₃@RGO, which achieves 80% degradation of RhB in 100 min under simulated solar light irradiation (Fig. 7d) and the rate constant κ (Fig. 7f) is about 2.50 times of that of bare WO₃. When the amount of RGO increases from 1.2% to 2.4%, the WO₃@RGO composites share similar morphology and almost same specific surface area but present decreasing photocatalytic performance, suggesting the content of RGO should be in a proper percentage. When the amount of RGO reaches 4.8%, the photocatalytic performance is declined obviously. Besides the microspheres shown in Fig. 6d, the WO₃ nanoflowers tightly wrapped and the nanobelts encircled by abundant RGO are also observed in the 4.8% WO₃@RGO from the TEM images in Fig. S5. When abundant black graphene was introduced, it would lead to shielding of the active sites on the catalyst surface and also rapidly decrease of the light intensity through the depth of the reaction solution (the so-called “shielding effect”).[41,46,47] Thereby, besides the decreased specific surface area and adsorption rate, the shielding effect caused by the abundant RGO should be one important cause which leads to the decreased performance. Therefore, it indicates that a suitable content of RGO is crucial for optimizing the photocatalytic activity of composite photocatalysts. In summary, the strategy of introducing proper content of RGO and then forming the 3D WO₃ hierarchical

nanostructure assembled with RGO closely wrapped nanobelts could greatly improve the photocatalytic performance.

The separation efficiency of photogenerated electrons and holes has a significant influence on the photocatalytic performance.[48] Therefore, the photoelectrochemical performances of the bare WO_3 and graphene- WO_3 composites photoelectrodes were studied using photocurrent-time curves. As shown in Figure 9, the variation of photocurrent matches well with the change of photocatalytic performance. It can be seen that 1.2% $\text{WO}_3@\text{RGO}$ shows the highest photocurrent response among all the samples, which is 3 times as high as that of the bare WO_3 . Such a high photocurrent means a much quicker migration rate and a higher separation efficiency of photo-generated carriers, thus leading to its high efficiency of photodegrading RhB or phenol.

3.3. Mechanism of enhancement of photocatalytic activity

In order to explore the photocatalytic mechanism of the 1.2% $\text{WO}_3@\text{RGO}$, the ESR spin-trap technique and the trapping experiments were used to investigate the main oxidative species during the photodegradation process.[48] Fig. 10a shows the ESR signals of the $\text{DMPO} \cdot \text{O}_2^-$ (DMPO , 5,5-dimethyl-1-pyrroline N-oxide, a nitron spin trap generally used for trapping radicals) for the bare WO_3 and 1.2% $\text{WO}_3@\text{RGO}$, from which six characteristic peaks of the $\text{DMPO} \cdot \text{O}_2^-$ adducts can be observed. It is obvious that both the bare WO_3 and 1.2% $\text{WO}_3@\text{RGO}$ can generate O_2^- radicals after irradiation. The bare WO_3 can utilize oxygen perhaps due to its 3D hierarchical structure assembled with 1D nanobelts which can quicken the charge transfer, since the bulk WO_3 hardly generates O_2^- radicals.[49] The characteristic four peaks of the $\text{DMPO} \cdot \text{OH}$ adduct with intensity 1:2:2:1 can be observed both in the bare WO_3 and 1.2% $\text{WO}_3@\text{RGO}$ after irradiation. The

stronger intensity of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radical peaks of 1.2% $\text{WO}_3@\text{RGO}$ as compared to bare WO_3 are observed, i.e. more $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals are generated on the surface of 1.2% $\text{WO}_3@\text{RGO}$ than that of bare WO_3 . The strong ESR signals of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ in the 1.2% $\text{WO}_3@\text{RGO}$ suggest that the strategy of intimately wrapping the nanobelts in WO_3 hierarchical structure by RGO is beneficial for the production of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$. It is well known that the abundant reactive oxygen species ($\bullet\text{OH}$ and $\bullet\text{O}_2^-$), which were identified as one of the most active initiators of photocatalytic degradation of organic contaminants, can be beneficial to the enhancement of photocatalytic activity.[31] Meanwhile, Fig. S11 shows that the ESR signal of $\bullet\text{OH}$ is much stronger than that of $\bullet\text{O}_2^-$ in the 1.2% $\text{WO}_3@\text{RGO}$, suggesting that $\bullet\text{OH}$ may be the main reactive oxygen species. It can be further confirmed through the trapping experiments using t-BuOH ($\bullet\text{OH}$ scavenger),[48] EDTA-2Na (hole scavenger)[48] and p-benzoquinone ($\bullet\text{O}_2^-$ scavenger),[50] respectively. Fig. 10c shows that the photodegradation process could be greatly prevented when adding EDTA-2Na and t-BuOH, while the addition of p-benzoquinone causes a small change on the photocatalytic performance. The results suggest that the $\bullet\text{OH}$ and holes should be the main reactive species in the process of photodegradation of RhB over the 1.2% $\text{WO}_3@\text{RGO}$. Moreover, after 100 min irradiation, the maximum peak of the solution gradually shifts from 554 nm to 531 nm (see Fig. 10d), indicating that the degradation of RhB is mainly caused by de-ethylation.[51]

Based on the above results, a tentative mechanism of the photocatalytic reaction is proposed in Scheme 2. Under solar light irradiation, electrons (e^-) are excited from the valence band (VB) to the conduction band (CB) of the WO_3 semiconductor and leave holes (h^+) in the VB. Then the electrons may transfer in the following four routines: I) to the surface of WO_3 nanobelts; II) to the carbon atoms on the thin RGO wrapping WO_3 nanobelts; III) to the carbon atoms on the RGO or GO

wrapping the mainframe of WO_3 microspheres or nanoflowers; IV) recombination with the holes in the forbidden band. Subsequently, the charge carriers (e^- and h^+) can form reactive oxygen species on the surface of the photocatalyst. Typically, the photogenerated electrons combine with the adsorbed oxygen to form $\bullet\text{O}_2^-$, and the holes react with OH^- to form $\bullet\text{OH}$. The photogenerated charge carriers or reactive oxygen species will react with reactants. Thus, the pollutants can be degraded during this process. As illustrated in Scheme 2, the electron transfer in the bare WO_3 can be realized by two ways (i.e., routines I and IV) with a high recombination rate, leading to a low photocatalytic performance. The WO_3/GO is similar to the bare WO_3 except that the electrons may be transferred by the third way (routine III) (Scheme 2b). But routine III may be unavailable since GO usually has low conductivity. The performance of the HyWO_3/GO could also be illustrated by Scheme 2b, since the aggregated RGO in the RGO-WO_3 nanoflowers network is less efficient in transferring electrons than the thin RGO sheets on the surface of microspheres in WO_3/RGO and the RGO closely wrapping the nanobelts in $\text{WO}_3@\text{RGO}$. Moreover, only the $\text{WO}_3@\text{RGO}$ composites have the second way (routine II) of transferring electrons to the closely wrapping RGO, resulting in a lowest recombination rate among the four composites as shown in Scheme 2d. In general, RGO can serve as an electron collector and transporter to separate the photogenerated electron-hole pairs efficiently, lengthening the lifetime of the charge carriers effectively, based on a good interaction between RGO and semiconductor. The WO_3 hierarchical structure assembled with RGO closely wrapped nanobelts is remarkably favored for the charge carriers transfer, leading to the high photocatalytic performance.

4. Conclusion

A high efficiency of the photocatalytic pollutant degradation under simulated solar light irradiation

has been achieved by RGO 3D wrapped WO₃ hierarchical nanostructure photocatalyst (WO₃@RGO) synthesized via a one-step hydrothermal method. The 1D building blocks of WO₃ hierarchical nanostructure were closely wrapped by a layer of RGO in the WO₃@RGO. When the mainframe of WO₃ hierarchical structure is wrapped by RGO or GO, due to the gaps between the 2D RGO sheet and the semiconductor, the photocatalytic performance cannot be improved effectively. While perfectly wrapping the WO₃ nanobelts by RGO could ensure an excellent interaction between the RGO and WO₃, facilitating the separation of electron and holes and the generation of abundant •OH and •O₂⁻ radicals and thus remarkably enhancing the photocatalytic performance. Moreover, the content of RGO is also crucial for the improvement of photocatalytic performance and the optimal performance is found in the 1.2% WO₃@RGO. The mechanism investigation shows that the 1.2% WO₃@RGO could generate more •OH and •O₂⁻ radicals than the bare WO₃ and the •OH and holes should be the main reactive oxidative species. It is expected that such a unique structure will be useful in environment remediation and energy conversion.

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Caption of Figures

Fig. 1. XRD patterns of the GO, WO₃ and 1.2% WO₃@RGO.

Fig. 2. XPS spectra of (a) C 1s of GO; (b) C 1s, (c) W 4f and (d) O 1s of the 1.2% WO₃@RGO.

Fig. 3. SEM images of (a) the bare WO₃; (b-d) 1.2% WO₃@RGO; (e) WO₃/GO; (f-g) HyWO₃/GO; (h) WO₃/RGO.

Fig. 4. TEM images of (a) GO, (b) the nanowires in the microsphere of the bare WO₃, (c) the 1.2% WO₃@RGO with two kinds of morphology and its corresponding enlarged images of (d) the microsphere and (e) the nanoflowers (the ellipses infer the agglomerated RGO); (f) HRTEM images of nanowires in the 1.2% WO₃@RGO and (g) the enlarged image of rectangular region, (h) bare WO₃ and (i) HyWO₃/GO.

Scheme 1. Illustration of different contact types between RGO or GO and WO₃ and the formation of (a) bare WO₃; (b) 1.2% WO₃@RGO; (c) WO₃/GO, WO₃/RGO and HyWO₃/GO; (d) illustration of the mainframe of WO₃ hierarchical structure wrapped by RGO or GO (I) and the WO₃ hierarchical structure 3D wrapped by RGO (II).

Fig. 5. Raman spectra of the GO, WO₃/GO, WO₃/RGO, HyWO₃/GO and 1.2% WO₃@RGO.

Fig. 6. SEM images of the 0.6%, 1.8%, 2.4% and 4.8% WO₃@RGO.

Fig. 7. Photocatalytic degradation of RhB by (a-c) the bare WO₃, WO₃/GO, HyWO₃/GO, WO₃/RGO and WO₃@RGO composites (the four composites have the same amount of GO or RGO: x=1.2%) and (d-f) the WO₃@RGO composites with different loading amounts of RGO. (All the results were the average of three parallel tests)

Fig. 8. Photocatalytic degradation of phenol by the bare WO₃, HyWO₃/GO, WO₃/RGO and 1.2%

WO₃@RGO composites.

Fig. 9. The photocurrent response of (a) the bare WO₃, WO₃/GO, HyWO₃/GO, WO₃/RGO and 1.2% WO₃@RGO composites; (b) the WO₃@RGO composites with different loading amounts of RGO.

Fig. 10. ESR signals of (a) the DMPO-•O₂⁻ in the methanol, (b) the DMPO-•OH in the aqueous dispersion under simulated solar light at room temperature; (c) The plots of photogenerated carriers trapping in the system of photodegradation of RhB over the 1.2% WO₃@RGO under simulated solar light; (d) temporal UV-Vis absorption spectral changes for the RhB solution (20 mg/L) over 1.2% WO₃@RGO as a function of simulated solar light irradiation time from 0 to 100 min.

Scheme 2. Illustration of the charge separation and transfer in the (a) bare WO₃; (b) WO₃/GO and HyWO₃/GO; (c) WO₃/RGO and (d) WO₃@RGO under solar light irradiation.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

Fig.8

Fig.9

Fig.10

bare WO_3

WO_3/GO or $HyWO_3/GO$

WO_3/RGO

$WO_3@RGO$