Construction of $\text{SnS}_2\text{--SnO}_2$ heterojunctions decorated on graphene nanosheets with enhanced visible-light photocatalytic performance

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Heterostructures formed by the growth of one kind of nanomaterial in/on another have attracted increasing attention due to their microstructural characteristics and potential applications. In this work, $\text{SnS}_2\text{--SnO}_2$ heterostructures were successfully prepared by a facile hydrothermal method. Due to the enhanced visible-light absorption and efficient separation of photo-generated holes and electrons, the $\text{SnS}_2\text{--SnO}_2$ heterostructures display excellent photocatalytic performance for the degradation of rhodamine (RhB) under visible-light irradiation. Additionally, it is found that the introduction of graphene into the heterostructures further improved photocatalytic activity and stability. In particular, the optimized $\text{SnS}_2\text{--SnO}_2/\text{graphene}$ photocatalyst can degrade 97.1% of RhB within 60 min, which is about 1.38 times greater than that of $\text{SnS}_2\text{--SnO}_2$ heterostructures. This enhanced photocatalytic activity could be attributed to the high surface area and the excellent electron accepting and transporting properties of graphene, which served as an acceptor of the generated electrons to suppress charge recombination. These results provide a new insight for the design and development of hybrid photocatalysts.

1. Introduction

Since TiO_2 was used to oxidize and decompose organic pollutants, semiconductor photocatalysis had attracted much attention from scientists around the world (Xiang *et al.*, 2015). Stable cheap and high-performance semiconductor photocatalysts are the basis of photocatalytic applications (Tian *et al.*, 2018). In recent years, various semiconductor nanomaterials have been explored as photocatalysts, for example, TiO_2 (Ye *et al.*, 2018; Xu *et al.*, 2010), ZnO (Samadi *et al.*, 2019), CdS (Deng *et al.*, 2019) and BiOCO_3 (Liang *et al.*, 2014). As a typical n-type semiconductor, SnO_2 has become one of the representatives of semiconductor photocatalysts due to its nontoxicity, low cost and excellent optical electrical properties (Park *et al.*, 2014). For instance, Liu *et al.* (2013) found that SnO_2 quantum dots with a diameter of 3–5 nm displayed an excellent photodegradation efficiency of the organic dye methylene blue (MB), even better than that of commercial P25. Seema *et al.* (2012) reported that the $\text{SnO}_2/\text{graphene}$ composite exhibited an enhanced catalytic degradation performance for MB under sunlight irradiation. However, SnO_2 is a wide-band semiconductor (~ 3.6 eV) and it can only absorb ultraviolet light. Additionally, the photoinduced carriers in SnO_2 is easy to be recombined, which inevitably reduces the photocatalytic performance of SnO_2 (Xin *et al.*, 2013; Mazloom *et al.*, 2015; Ali *et al.*, 2015).

To further enhance the photocatalytic performance of SnO_2 , many new methods were developed, including creating heterojunctions (Ahmed *et al.*, 2017; Babu *et al.*, 2017; Marschall, 2014; Li *et al.*, 2016), precious metal deposition (Dhakshinamoorthy *et al.*, 2016), semiconductor photosensitization (Booshehri *et al.*, 2017) and ion doping (Tian *et al.*, 2016; Tan *et al.*, 2015; Rajabi & Farsi, 2015). Among these, the design and synthesis of heterojunctions is an effective way to improve the photocatalytic performance of semiconductors. This is because the heterojunction photocatalyst cannot only reduce the carrier recombination rate and accelerate the electron transfer speed (Khan & Berk, 2013; Zhou *et al.*, 2015), but can also widen the absorption of the solar spectrum to visible-light regions (Brandt *et al.*, 2015; Li *et al.*, 2017a). Recently, Gao *et al.* (2018) reported the controlled synthesis of Sb-doped SnO_2 -decorated porous g- C_3N_4 nanosheet composites. Due to their osculating interfacial contact, the formed heterojunction between g- C_3N_4 and Sb-doped SnO_2 significantly improved the separation of the photogenerated charge carriers, and therefore increased the degradation of rhodamine B under visible-light irradiation. Zhang *et al.* (2011a) synthesized $\text{SnS}_2/\text{SnO}_2$ heterojunctions *via* the *in-situ* oxidation of SnS_2 nanoparticles by H_2O_2 . The as-prepared $\text{SnS}_2/\text{SnO}_2$ nanocomposites with an optimized mass ratio displayed better photocatalytic activity and stability than pure SnS_2 nanoparticles. Yao and co-authors (Xu *et al.*, 2015) prepared the SnO_2 - SnS_2 heterojunctions by a hydrothermal oxidation method. They found that the coupled band-gap structure of SnO_2 - SnS_2 heterojunctions facilitates the interfacial electron transfer and abates the self-radiative recombination of charges.

Although the SnS_2 - SnO_2 heterojunction photocatalysts are beneficial for improving the photocatalytic properties of semiconductor materials, their low surface-to-volume ratio always results in unsatisfactory adsorptivity, conductivity and catalytic activity sites (Yin *et al.*, 2017). Graphene is an atomic sheet of sp^2 -bonded C atoms that are arranged in a honeycomb structure (Guo *et al.*, 2013) and is highly appreciated owing to its merits of superior electronic properties, high specific surface area and remarkable structural flexibility. In this regard, the combination of SnS_2 - SnO_2 heterojunctions and graphene is a promising way to attain better catalytic performance for the following reasons: (i) the graphene in the hybrids can serve as an acceptor of the photo-excited electrons and effectively suppress the charge recombination, leaving more charge carriers to form reactive species and promote the degradation of dyes (La *et al.*, 2017); (ii) the rapid transport of charge carriers could be achieved and an effective charge separation subsequently accomplished due to the excellent conductivity of graphene. In the present work, SnS_2 - SnO_2 /graphene nanocomposites were rationally designed and synthesized by a two-step hydrothermal method. Due to the enhanced visible-light absorption and efficient separation of photogenerated holes and electrons, the optimized SnS_2 - SnO_2 /graphene heterojunction photocatalyst can degrade 97.1% of rhodamine (RhB) under visible-light irradiation within 60 min, which is much better than pure graphene, SnO_2

and the SnS_2 - SnO_2 heterostructures. These results provide a new insight for the design and development of hybrid photocatalysts.

2. Experimental

2.1. Synthesis of SnS_2 - SnO_2 heterostructures

The SnS_2 - SnO_2 heterostructures were prepared by a one-step hydrothermal method (Zhang *et al.*, 2014). In a typical synthesis, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (5.0 mmol) and CH_3CSNH_2 (7.5 mmol) were dissolved in deionized water (40 ml) with vigorous stirring at room temperature. The resulting suspension was transferred into a 50 ml Teflon-lined autoclave. The autoclave was placed in an oven and hydrothermal reactions at 190 °C were allowed to occur for 3, 6 and 9 h, respectively. After being cooled to room temperature naturally, the three products were rinsed several times with distilled water and ethanol, and then dried at 60 °C for 10 h. The three products are labelled as SnS_2 - SnO_2 -3, SnS_2 - SnO_2 -6 and SnS_2 - SnO_2 -9, respectively. Pure SnO_2 and SnS_2 were also prepared by a similar procedure, as mentioned above.

2.2. Preparation of SnS_2 - SnO_2 /graphene photocatalysts

Graphene oxide (GO) was prepared by a modified Hummers method (Ullah *et al.*, 2017). The reduced graphene oxide (RGO) was then obtained by annealing the as-prepared GO power at 500 °C for 1 h under an N_2 atmosphere. SnS_2 - SnO_2 /RGO nanocomposites were synthesized *via* a simple one-step hydrothermal procedure. In a typical synthesis, the as-prepared RGO (50 mg) was dispersed in distilled water (50 ml) by ultrasonication. The above prefabricated SnS_2 - SnO_2 heterostructures were then added to the RGO suspension and stirred for 1 h. Subsequently, the obtained mixture was transferred to a 50 ml Teflon-lined autoclave, which was placed in an oven and hydrothermal reaction at 180 °C was allowed to occur for 24 h. After cooling to room temperature naturally, the three products were rinsed several times with distilled water and ethanol, and then dried at 60 °C for 10 h in a vacuum oven. The obtained products are labelled SnS_2 - SnO_2 -3/RGO, SnS_2 - SnO_2 -6/RGO and SnS_2 - SnO_2 -9/RGO, respectively.

2.3. Microstructure characterization

The crystallinity of the as-prepared SnS_2 - SnO_2 /RGO composites was investigated by X-ray diffraction (XRD, Rigaku D/MAX-2500, Cu $K\alpha$, 40 kV, 40 mA) at a scanning rate of 8° min⁻¹. The morphologies of the SnS_2 - SnO_2 /RGO composites were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6700F, 5 kV) and transmission electron microscopy (TEM, 200CX, 200 kV). High-resolution transmission electron microscopy (HRTEM) observations were performed on a JEOL JEM-2100F electron microscope operating at 200 kV. UV-Vis diffuse reflectance spectra (DRS) of the samples were obtained with a Hitachi U4100 UV Spectrometer. A Hitachi F-2700 fluorescence spectrophotometer was used to record the photoluminescence

(PL) spectra. X-ray photoelectron spectroscopy (XPS) was conducted using an X-ray photoelectron spectrometer with monochromated Al $K\alpha$ radiation. Raman spectra were recorded on a Renishaw inVia. The graphene contents in the nanocomposites were determined *via* thermogravimetric analysis (TGA, SDT Q600 TG/DTA) in air at temperatures ranging from room temperature to 1100 °C.

2.4. Photocatalytic performances

Rhodamine B (RhB) was employed as a model compound to evaluate the photocatalytic activity of the as-prepared composites. In detail, the catalyst (10 mg) was dispersed in RhB solution (20 ml, 100 mg l⁻¹) and stirred magnetically for 30 min in the dark to ensure an adsorption-desorption balance between the photocatalyst and RhB. The reactor was then exposed under a 500 W Xenon lamp with a UV-cutoff filter ($\lambda > 420$ nm). At a given time interval, 1 ml of solution was taken from the suspension and diluted to 3.0 ml, which was immediately centrifuged at 8000 rpm for 5 min. The UV-Vis spectra of the centrifuged solution were then recorded using a UV-4100 spectrophotometer. Each photocatalytic experiment was repeated three times and exhibited a good reproducibility, with relative average deviations of <3% for all the repeated photocatalytic experiments.

3. Results and discussion

The X-ray diffraction (XRD) patterns of the RGO, SnO₂, SnS₂-SnO₂-6 and SnS₂-SnO₂/RGO samples are presented in Fig. 1. For pure RGO, the diffraction peak at $2\theta = 25.9^\circ$ can be attributed to the carbon (002) plane of the graphene nanosheets. The as-prepared SnO₂ is ascribed to the tetragonal phase SnO₂, having lattice constants $a = b = 4.738$ Å and $c = 3.187$ Å (JCPDS 41-1445). The diffraction peaks at 26.6, 33.9 and 51.8° correspond to the (110), (101) and (211) faces of SnO₂. When SnO₂ is coupled with SnS₂, the characteristic

peaks of SnO₂ at 26.6, 33.9 and 51.8° are still observed clearly. New peaks appearing at 15.0, 28.2, 32.1 and 50.0° are attributed to the (001), (100), (101) and (110) planes of hexagonal phase SnS₂ (JCPDS 23-0677, $a = b = 3.648$ Å and $c = 5.899$ Å), respectively. The SnS₂-SnO₂/RGO nanocomposites showed a similar XRD pattern to the SnS₂-SnO₂ heterojunctions. No diffraction peaks for graphene were observed, which might be due to the low amount and relatively low diffraction intensity of graphene. In addition, it is found that the intensity of the (101) peak belonging to SnS₂ dwindles and the intensity of the (101) peak belonged to SnO₂ increases with increasing hydrothermal reaction time from 3 to 9 h. These results indicate that a suitable hydrothermal time is beneficial for synergies between the heterojunction and grain size of SnS₂ and SnO₂ for effective photocatalytic degradation when the SnS₂-SnO₂/graphene nanocomposites were used as photocatalysts.

Raman analysis is known to be a more surface-sensitive technique for assessing chemical states. Fig. 2 shows the Raman spectra of the as-prepared RGO and SnO₂-SnS₂/RGO nanocomposites with different hydrothermal reaction times.

Figure 1

XRD patterns of the as-prepared samples of (a) pure RGO, (b) SnO₂ nanoparticles, (c) SnO₂-SnS₂-6, (d) SnO₂-SnS₂-3/RGO, (e) SnO₂-SnS₂-6/RGO and (f) SnO₂-SnS₂-9/RGO.

Figure 2

Raman spectra of the as-prepared pure RGO and SnO₂-SnS₂/RGO nanocomposites.

Figure 3

XPS spectra for the $\text{SnO}_2\text{-SnS}_2\text{-6/RGO}$ sample, showing (a) a survey and high-resolution spectrum of O 1s, and high-resolution spectra of (b) C 1s, (c) S 2p and (d) Sn 3d.

As shown in Fig. 2(a), two characteristic vibration peaks are observed from 1000 to 2000 cm^{-1} . The strong peak centred at 1329 cm^{-1} is assigned to the disorder band associated with structural defects generated in graphene (D band), while the peak centred at 1590 cm^{-1} corresponds to the well-ordered E_{2g} phonon scattering of sp^2 C atoms of graphene (G band) (Li *et al.*, 2017b). The intensity ratio of the D and G peaks (I_D/I_G) was then used to explore the physicochemical properties of the sample. The I_D/I_G ratios of pure RGO, $\text{SnO}_2\text{-SnS}_2\text{-3/RGO}$, $\text{SnO}_2\text{-SnS}_2\text{-6/RGO}$ and $\text{SnO}_2\text{-SnS}_2\text{-9/RGO}$ are 1.42, 1.27, 1.34 and 1.23, respectively. In addition, the strong characteristic vibration peak appearing in $\text{SnO}_2\text{-SnS}_2\text{/RGO}$ samples at 331 cm^{-1} is assigned to the A_{1g} vibration model of SnS_2 , as seen in Fig. 2(b). It is found that the A_{1g} vibration model of SnS_2 in the $\text{SnO}_2\text{-SnS}_2\text{-6/RGO}$ sample is decreased compared to that of $\text{SnO}_2\text{-SnS}_2\text{-3/RGO}$, and the tendency is similar to the $\text{SnO}_2\text{-SnS}_2\text{-9/RGO}$ sample. This result means that increasing the hydrothermal time is beneficial for the oriented growth of the SnS_2 and SnO_2 heterojunctions, which provides a facile method for tuning the photocatalytic performance of the hybrids. Thermogravimetric analysis (TGA) was employed to measure the graphene contents in the

$\text{SnO}_2\text{-SnS}_2\text{-6/RGO}$ sample (Fig. S1 in the supporting information). After thermal oxidation in air, SnS_2 was oxidized to SnO_2 and the product remaining after TG measurement was pure SnO_2 . In this regard, the content of RGO in $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ was calculated to be 8.06 wt% by comparing the TG curves of $\text{SnS}_2\text{-SnO}_2\text{-6}$ and $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$. Additionally, as shown in Fig. S1(b) (see supporting information), RGO is rather stable until the temperature reaches 500 $^\circ\text{C}$, which is consistent with our conclusion.

An X-ray photoelectron spectroscopy (XPS) analysis was then conducted to analyze the chemical states of the Sn, O, S and C elements in the $\text{SnO}_2\text{-SnS}_2\text{-6/RGO}$ sample. Fig. 3(a) gives a fully scanned spectrum and the O 1s XPS peak of the $\text{SnO}_2\text{-SnS}_2\text{-6/RGO}$ sample. The observed O 1s peak at 531.3 eV can be assigned to lattice oxygen in crystalline SnO_2 (Chen *et al.*, 2014). The spectrum of C 1s, as shown in Fig. 3(b), displays binding energies at 284.5, 285.6 and 286.8 eV, which are assigned to C—C, C—O and C=O, respectively (Guo *et al.*, 2017). The decreased intensity of the carbon binding to oxygen in the sample suggests that most oxygen-containing functional groups in layered graphene oxide have been reduced to RGO. The peaks as shown in Fig. 3(c) centred at

Figure 4
(a)/(b) FE-SEM and (c)/(d) TEM images of the as-prepared (a)/(c) $\text{SnS}_2\text{-SnO}_2\text{-6}$ and (b)/(d) $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ samples. (e) HRTEM image and (f) SAED pattern of the $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ sample.

161.8 and 163.1 eV can be assigned to S 2p (Ou *et al.*, 2015). Fig. 3(d) depicts the XPS spectrum of Sn 3d. The two peaks located at 487.0 and 495.5 eV correspond to the Sn 3d_{5/2} and Sn 3d_{3/2} binding energies of Sn⁴⁺ in SnO₂ and SnS₂, respectively (Li *et al.*, 2014). The above results demonstrate that the as-prepared samples are indeed composed of SnO₂, SnS₂ and graphene.

The field emission scanning electron microscopy (FE-SEM) images shown in Fig. 4(a) indicate that the $\text{SnS}_2\text{-SnO}_2$ heterojunctions are irregular aggregates composed of plate-like SnS₂ covered by tiny particle-like SnO₂. Detailed microstructure analysis indicates that the SnO₂ morphology comprises nanoparticles with diameters of 2–5 nm, and the SnS₂ morphology comprises nanoplates with a planar size of 50–100 nm. After the introduction of graphene, it can be seen that the average size of the irregular aggregates decreases (Fig. 4b). In addition, some irregular sheet-like morphologies can be observed, confirming the existence of graphene in the sample. The thermogravimetric analysis is shown in Fig. S1 in the supporting information. Figs. 4(c) and 4(d) show the transmission electron microscopy (TEM) images of the $\text{SnS}_2\text{-SnO}_2$ and $\text{SnS}_2\text{-SnO}_2\text{/graphene}$ samples, respectively. One can see that the SnO₂ nanoparticles are deposited on the surface of SnS₂ nanoplates. No individual SnO₂ nanoparticle or SnS₂ nanoplate can be found, implying that the $\text{SnS}_2\text{-SnO}_2$ heterojunctions were created by the growth of SnO₂ nanocrystals on SnS₂ nanoplates. The gray contrast seen in Fig. 4(d) further illustrates that the $\text{SnS}_2\text{-SnO}_2$ heterojunctions are maintained on the graphene sheets by deposition and reduction. This distribution of plate-like SnS₂ and particle-like SnO₂ morphologies decreases the restacking of graphene nanosheets and increases the stability of individual graphene nanosheets, which is expected to exhibit better photocatalytic

performance (Khan *et al.*, 2016). The microstructure of the $\text{SnS}_2\text{-SnO}_2\text{/graphene}$ nanocomposites was further characterized by high-resolution TEM imaging techniques (Fig. 4e). This reveals that the nanosheets display lattice fringes of 0.589 and 0.316 nm, which correspond to the lattice spacings of the (001) and (100) crystal planes, respectively, of hexagonal SnS₂. The smaller-sized nanoparticles display a lattice fringe of 0.334 nm, which corresponds to the lattice spacing of the (110) crystal plane of tetragonal SnO₂. The (100) and (001) planes of SnS₂ are close to the (110) plane of SnO₂, suggesting the formation of a heterojunction between SnS₂ and SnO₂. Therefore, the HRTEM results demonstrated that the $\text{SnS}_2\text{-SnO}_2\text{-6/graphene}$ sample is constructed of SnS₂ nanosheets modified with smaller-size SnO₂ nanoparticles on the surface of graphene. The selected area electron diffraction (SAED) pattern, as shown in Fig. 4(f), provides further proof of the formation of the crystalline phases SnO₂ (marked as white bright spots) and SnS₂ (marked as yellow bright spots).

As shown in the N₂ adsorption–desorption isotherms of SnO₂, SnS₂, $\text{SnS}_2\text{-SnO}_2\text{-6}$ and $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ (Fig. 5a), the $\text{SnS}_2\text{-SnO}_2\text{-6}$ and $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ samples exhibit a type-IV curve with a distinct hysteresis loop at a relative pressure (p/p_0) of 0.4–1.0, indicating the characteristics of a mesoporous structure. The $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ sample has a Brunauer–Emmett–Teller (BET) surface area of 107.69 m² g^{−1}, which is much greater than that of the $\text{SnS}_2\text{-SnO}_2\text{-6}$ sample (66.58 m² g^{−1}). The enhanced BET surface is mainly attributed to the contribution of RGO and the unique composite architecture. The desorption isotherm obtained *via* the Barrett–Joyner–Halenda method was used to calculate the pore-size distribution (Fig. 5b). It is demonstrated that the $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ sample has a large mesopore centred mainly at 3.98 nm, suggesting that some parts of the small

Figure 5
(a) N_2 adsorption-desorption isotherm and (b) pore diameter distribution of the as-prepared SnO_2 , SnS_2 , $\text{SnS}_2\text{-SnO}_2\text{-6}$ and $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ samples.

holes have collapsed (Mishra *et al.*, 2015). The smaller pore-size mesoporous structure in $\text{SnS}_2\text{-SnO}_2\text{-6/graphene}$ facilitate photon diffusion to active sites with less resistance, leading to efficient separation of photo-generated holes and electrons, which is conducive to the improvement of photocatalytic performance (Liu *et al.*, 2014).

The UV-Vis diffuse reflectance spectra (DRS) of the SnO_2 , SnS_2 , $\text{SnS}_2\text{-SnO}_2\text{-6}$ and $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ samples are shown in Fig. 6(a). Since pure SnO_2 can absorb solar energy at wavelengths shorter than 400 nm, our experimental results are consistent with the previous report of Zhang *et al.* (2016b). It is clearly seen that visible-light absorption is enhanced after the addition of SnS_2 . The visible-light absorption further increases for the $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ sample, indicating the positive effect of graphene. The improved photocatalytic activity is due to the absorption range of the $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ sample extending into visible-light absorption. Moreover, there was an obvious red shift in the absorption edge of $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ compared to $\text{SnS}_2\text{-SnO}_2\text{-6}$. This indicated that the narrowing of the band gap of the $\text{SnS}_2\text{-SnO}_2$ heterojunctions occurred with the introduction of graphene. As a result, a more efficient utilization of the solar spectrum could be

achieved, resulting in significant improvement in the photocatalytic performance under visible-light irradiation.

The temporal evolution of the UV-Vis absorption spectra of RhB during the photocatalytic reaction for all samples are presented in Fig. 6(b). One can see that most of the dye molecules (*ca* 93%) remained in the solution with pure SnO_2 as the catalyst after equilibrium in the dark for 40 min, whereas 16% of dye molecules were adsorbed on the surface of $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$. Obviously, $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ showed the best adsorption strength among the six catalysts. Additionally, only 13 and 11% RhB were degraded under visible-light irradiation within 60 min for RGO and SnO_2 , respectively, which is significantly lower than for $\text{SnS}_2\text{-SnO}_2\text{-6}$ (84%) and $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ (97%). Discernable differences in the photocatalytic performance is mainly due to the enhanced adsorptivity, extended light-absorption range, and enhanced charge separation and transportation due to the introduction of graphene and the formation of heterojunctions (Veldurthi *et al.*, 2018). Firstly, graphene has been demonstrated to be a promising candidate as an acceptor material due to its unique two-dimensional π -conjugation structure. In this regard, graphene can serve as an acceptor of the generated electrons to suppress charge recombination, leaving more charge carriers to form reactive species and promote the degradation of dyes. Therefore, in our system, the excited electrons of the $\text{SnS}_2\text{-SnO}_2$ heterojunctions could transfer from the conduction band to graphene *via* a percolation mechanism. Additionally, the $\text{SnS}_2\text{-SnO}_2$ heterojunctions decorated on the surface of graphene enhance the visible-light absorption and accelerate the separation of photogenerated holes and electrons. Therefore, the $\text{SnS}_2\text{-SnO}_2\text{/RGO}$ photocatalysts ($\text{SnS}_2\text{-SnO}_2\text{-3/RGO}$, $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ and $\text{SnS}_2\text{-SnO}_2\text{-9/RGO}$) show a much greater photocatalytic activity for RhB than pure SnO_2 and $\text{SnS}_2\text{-SnO}_2\text{-6}$. It is also much greater than the results reported in the literature (Zhang *et al.*, 2011a,b; Fakhri *et al.*, 2015). We further investigated the recyclability of the $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ sample, as shown in Fig. 6(d). It was observed that the $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ sample exhibits high photostability even over five cycles, as depicted in the photo-degradation plots.

To illustrate the advantages of the $\text{SnS}_2\text{-SnO}_2\text{/RGO}$ nanocomposites in catalyzing the degradation of RhB, the photoluminescent (PL) emission spectra were measured on an F-2700 spectrometer using a 325 nm line laser (Fig. 7a). Pure SnS_2 has an emission centred at ~ 508 nm due to the band-gap recombination of electron-hole pairs. In contrast, the obvious PL quenching in the $\text{SnO}_2\text{-SnS}_2$ heterojunctions suggests that the electron-hole pair recombination is greatly suppressed. Additionally, the PL intensity at ~ 508 nm further decreases after the introduction of graphene into the $\text{SnO}_2\text{-SnS}_2$ heterojunctions, demonstrating the efficient charge transfer between the graphene and the heterojunctions (Annamalai *et al.*, 2015). The improved charge-separation behaviour is further supported by the transient photocurrent experiments tested for SnS_2 , SnO_2 and $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ samples, as shown in Fig. 7(b). It is clear that the photocurrent response of SnS_2 and SnO_2 is negligible due to the slow charge transfer

Figure 6

(a) UV-Vis spectrum of the as-synthesized SnO₂, SnS₂, SnS₂-SnO₂-6 and SnS₂-SnO₂-6/RGO samples. (b) Photocatalytic degradation efficiencies of RhB using different catalysts. (c) Evolution of the UV-Vis absorption spectra during the course of reduction of RhB using SnS₂-SnO₂-6/RGO as the photocatalyst. (d) Photocatalytic degradation of RhB for five cycles using the SnS₂-SnO₂-6/RGO sample.

and heavy charge recombination, while the photocurrent response of the SnS₂-SnO₂-6/RGO sample is approximately four times greater than that of SnS₂ and SnO₂. The improvement of photocurrent indicates that the suppression of charge recombination is significantly improved due to the irreversible electron transfer through the SnS₂-SnO₂ heterojunction (Lang *et al.*, 2015). The cyclic voltammetry (CV) measurements were also carried out with a three-electrode system (Fig. 7c). The results reflect that SnO₂ has a lower CV current due to its poor electrical conductivity and electroactivity. The SnS₂-SnO₂-6 heterostructures have a larger current of CV compared to SnO₂, which favours lower electron-hole recombination (Singh *et al.*, 2017). The SnS₂-SnO₂-6/RGO sample displayed the highest current because the graphene provides direct routes to accelerate the charge transport through the SnS₂-SnO₂ heterojunctions (Kumar *et al.*, 2016). The electrochemical impedance spectra (EIS) of the SnO₂, SnS₂-SnO₂-6 and SnS₂-SnO₂-6/RGO samples were evaluated using the same three-electrode system. The Nyquist plots are shown in Fig. 7(d), where the impedance spectra of the electrodes consist of a quasi-semicircle at higher frequency and a linear part at lower frequency. The semicircular portion is

related to the reaction occurring at the electrode-electrolyte interface, and the reaction is the charge-transfer impedance. If the diameter of the semicircle is smaller, the charge-transfer resistance will be smaller (Zhang *et al.*, 2016a). It can be seen that the SnS₂-SnO₂-6 sample shows an initial resistance of 80 Ω and the SnS₂-SnO₂-6/RGO sample shows an initial resistance of 46 Ω. The decrease of charge-transfer resistance indicates that the SnS₂-SnO₂-6/RGO sample has better electrical conductivity. Moreover, the straight line in the low frequency range reflects the transfer impedance of the substance (Chen *et al.*, 2017). A larger slope of the straight line implies a smaller transfer resistance of the substance. This indicates that the carrier lifetime of the SnS₂-SnO₂-6/RGO sample has been prolonged, with the introduction of graphene having improved the conduction of electrons. Therefore, the photocatalytic activity of the SnS₂-SnO₂-6/RGO sample is better than the SnS₂-SnO₂ heterostructures and pure SnO₂.

In order to further understand the photocatalytic mechanism of the SnS₂-SnO₂-6/RGO sample, *i.e.* whether the electrons and holes are separated efficiently and the active free radical plays a main role during the photocatalytic degradation of RhB, an active species trapping experiment

Figure 7

(a) Photoluminescence spectra, (b) transient photocurrent responses, (c) CV curves and (d) EIS Nyquist plots of the SnS_2 , $\text{SnS}_2\text{-SnO}_2\text{-6}$ and $\text{SnS}_2\text{-SnO}_2\text{-6/RGO}$ samples.

was carried out (Fig. S2 in the supporting information). The scavengers used in our work were *tert*-butyl alcohol (TBA) for $\cdot\text{OH}$, benzoquinone (BQ) for $\cdot\text{O}_2^-$ and disodium ethylenediaminetetraacetate (EDTA-2Na) for h^+ , which were added to the reaction system with a concentration of $\sim 1.5 \text{ mol l}^{-1}$. It is found that $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ are the main reactive species to degrade RhB, whereas h^+ does not play an important role under the decomposed reaction of RhB.

A possible photodegradation mechanism of $\text{SnS}_2\text{-SnO}_2/\text{graphene}$ nanocomposites under visible light is presented in Fig. 8. The existence of $\text{SnS}_2\text{-SnO}_2$ heterostructures on the surface of graphene can help to form a heterogeneous structure, providing a large surface and abundant interfaces. This unique structure favours an enhanced photocatalytic performance for the $\text{SnS}_2\text{-SnO}_2/\text{graphene}$ nanocomposites. Under the illumination of visible light on SnO_2 , the electrons from the valance band (E_v) are excited to its conduction band (E_c) and hence free electron-hole pairs will be generated (Lang *et al.*, 2015). For the $\text{SnS}_2\text{-SnO}_2$ heterostructures, these excited electrons directly from the conduction band (E_c) of SnS_2 are transferred to the conduction band (E_c) of SnO_2 due to its favourable Fermi level. Therefore, the presence of SnS_2 and the increased percentage composition more effectively mitigate the recombination of photogenerated electron pairs.

When an appropriate amount of graphene is introduced in the $\text{SnS}_2\text{-SnO}_2$ heterostructures to form a novel ternary semiconductor $\text{SnS}_2\text{-SnO}_2/\text{graphene}$ nanocomposite, the photo-

Figure 8

Schematic of the photocatalytic oxidation process and diagram of the energy band structure for the photocatalytic mechanism of $\text{SnS}_2\text{-SnO}_2/\text{graphene}$ nanocomposites with $\text{SnS}_2\text{-SnO}_2$ heterojunctions. E_c is the conduction band, E_f is the Fermi level, E_v is the valance band and E_g is the band-gap energy.

generated electrons are trapped and the quick recombination of the electron hole is reduced. When the photogenerated electron-hole pairs migrate to the surface of the SnS₂-SnO₂/graphene nanocomposites through the internal electric field of the SnS₂-SnO₂ and graphene, the photogenerated electrons react with dissolved O₂ producing the active 'O₂'. Meanwhile, the hydroxide ion derived from RhB forms 'OH and reacts with the photogenerated holes. These hydroxyl radicals together with oxygen peroxide radicals from the SnS₂-SnO₂/graphene nanocomposites give rise to the oxidative decomposition of RhB to H₂O, CO₂ and other mineralization substances (Zhang *et al.*, 2016b). The reaction mechanism can be summarized as follows:

4. Conclusions

In summary, SnS₂-SnO₂ heterojunctions assembled on graphene nanosheets were prepared by a two-step hydrothermal method. The results indicated that the SnS₂-SnO₂/graphene nanocomposites show enhanced photocatalytic activity for the degradation of organic pollutants. Interestingly, the decolorization rate of RhB by this ternary semiconductor nanocomposite with an optimized hydrothermal reaction time can reach 95.9% within 30 min, which was faster and more efficient than for the pure SnO₂, SnS₂ and SnS₂-SnO₂ heterostructures. An analysis of the photocatalytic mechanism indicated that the improved photocatalytic activity of the nanocomposites was derived from the enhanced visible-light absorption, efficient separation of photo-generated holes and electrons, as well as the excellent electron accepting and transporting properties of graphene.

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