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Article

Accelerating directional charge separation via built-in interfacial electric fields originating from work-function differences

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ABSTRACT

In this work, a hierarchical porous SnS₂/rGO/TiO₂ hollow sphere heterojunction that allows highly-efficient light utilization and shortening distance of charge transformation is rationally designed and synthesized. More importantly, an rGO interlayer is successfully embedded between the TiO₂ hollow sphere shells and outermost SnS₂ nanosheets. This interlayer functions as a bridge to connect the two light-harvesting semiconductors and acts as a hole injection layer in the tandem heterojunction. The induced built-in electric fields on both sides of the interface precisely regulate the spatial separation and directional migration of the photo-generated holes from the light-harvesting semiconductor to the rGO hole injection interlayer. These synergistic effects greatly prolong the lifetime of the photo-induced charge carriers. The optimized tandem heterojunction with a 2 wt% rGO loading demonstrate enhanced visible-light-driven photocatalytic activity for Rhodamine B (RhB) dye degradation (removal rate: 97.3%) and Cr(VI) reduction (removal rate: 97.09%). This work reveals a new strategy for the rational design and assembly of hollow-structured photocatalytic materials with spatially separated reduction and oxidation surfaces to achieve excellent photocatalytic performance.

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1. Introduction

Recently, water pollution caused by organic contaminants and heavy metals has posed a serious threat to human health, the ecosystem, and sustainable social development. Photocatalysis is considered to be an attractive potential strategy to solve these worsening environmental issues, due to its high efficiency, low cost, energy savings, and lack of secondary pollution [1–3]. Efficient light absorption, high charge separation,

and fast surface reaction kinetics are requisite properties for high-performance photocatalysts [4–8]. In this respect, porous TiO₂ hollow spheres are a promising candidate for the construction of systems with high photocatalytic activity, as they exhibit the following merits: (1) The raw material is inexpensive, non-toxic, and has a moderate redox potential and high thermal and chemical stability. (2) The hollow architecture not only adequately utilizes incident light through multiple light scattering, but also provides a large surface area that exposes

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abundant active sites. (3) Their porosity provides additional channels to enable mass transfer processes [7–11]. Nevertheless, hollow-structured TiO_2 presents the intrinsic drawbacks of narrow spectral absorption and inefficient separation and transport of photo-induced charge carriers, which significantly inhibits its practical applications [12–15].

Therefore, the design of broad-spectrum-responsive TiO_2 -based photocatalysts with good photocatalytic performance is important to achieve widespread and practical application. The construction of heterojunctions by coupling narrow-band-gap semiconductors has been demonstrated to be a powerful strategy to efficiently extend light absorption and promote charge separation. The indirect bandgap semiconductor SnS_2 has many inherent advantages, such as its narrow bandgap ($E_g = 2.18\text{--}2.44\text{ eV}$), low toxicity, excellent chemical stability, low cost, and wide spectral response [16–19]. Therefore, the combination of ultrathin SnS_2 nanosheets with porous TiO_2 hollow spheres should provide significant synergistic effects in terms of the photocatalytic performance of the heterojunction. The hierarchical hollow sphere structure is beneficial for visible light harvesting, while the ultrathin SnS_2 nanosheets have a shorter charge-diffusion length, thus efficiently inhibiting the internal recombination of the photo-excited charge carriers. However, due to the limitations of their energy band positions, type-I band alignments are easily formed in $\text{TiO}_2/\text{SnS}_2$ composites, which reduces their photocatalytic redox ability to a large extent. Additionally, the surviving photo-generated electrons and holes accumulated on the surfaces of the components have a high probability of random surface recombination. To overcome these limitations, the creation of an interfacial driving force to regulate charge separation and transfer is urgently needed.

To overcome the above-mentioned problems, embedding reduced graphene oxide (rGO) at the interface between TiO_2 and SnS_2 is thought to be a promising approach to precisely control the photo-excited electron or hole extraction via the formation of built-in electric fields on both sides of the interface [20–22]. For instance, Li et al. [23] employed a partially oxidized graphene (pGO) layer as an interfacial conduction layer in a $\text{CoPO}_3/\text{pGO}/\text{LDH}/\text{BiVO}_4$ photoanode; the pGO layer was crucial in facilitating the transfer of photo-induced holes from BiVO_4 to CoPO_3 . Dai et al. [22] have demonstrated that functionalized GO can act as an excellent hole-extraction material in heterojunctions to further improve device performance. Moreover, previous reports have indicated that the band structure, work function, conductivity, hydrophilicity, and optical properties of rGO can be readily tuned via chemical functionalization [24,25]. Thus, the use of different semiconductors with suitable energy levels on either side of rGO can effectively accelerate the spatial separation and directional migration of photo-induced charge carriers near the surface due to the potential gradients at the interfaces of the heterojunction.

Herein, we report the synthesis of a hierarchical porous $\text{SnS}_2/\text{rGO}/\text{TiO}_2$ hollow sphere heterojunction via a modified “silica-protected calcination” method. The hierarchical porous hollow sphere structure not only enhances the light-harvesting ability of the composite, but also provides abundant active sites

for the photoredox reaction. The rGO interlayer between the two light absorbers serves as an effective hole injection layer. The driving force derived from the built-in interfacial electric fields can effectively facilitate directional injection of the photo-induced holes from TiO_2 and SnS_2 to the rGO interlayer, thus retarding charge recombination. This special structural design spatially isolates the oxidation and reduction sites on the different materials, leading to a selective photoredox reaction surface. Compared to bare TiO_2 , SnS_2 , and binary $\text{SnS}_2/\text{TiO}_2$ composites, the optimal tandem heterojunction with a 2 wt% rGO loading exhibited significantly improved visible-light photocatalytic performance and durability in Rhodamine B (RhB) decomposition and Cr(VI) reduction.

2. Experimental

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd., were of analytical grade, and were used as received. The experimental details are provided in the Supporting Information.

2.1. Materials

All chemicals were of analytical grade and used as received. Tetraethyl orthosilicate (TEOS), ethanol, $\text{NH}_3\cdot\text{H}_2\text{O}$, $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (TBOT), acetonitrile, polyvinylpyrrolidone (PVP, K30), NaOH, γ -aminopropyl methyl diethoxysilane (APTES), $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$, L-cysteine, rhodamine B (RhB) and $\text{K}_2\text{Cr}_2\text{O}_7$ were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of SiO_2 nanospheres

SiO_2 nanospheres were synthesized by the modified Stöber's method [1]. In a typical synthesis, 10 mL H_2O , 5 mL $\text{NH}_3\cdot\text{H}_2\text{O}$ (28 wt%) and 50 mL ethanol were added into a conical flask. Then, 5 mL TEOS was slowly dropped into the mixed solution and magnetic stirred for 6 h at room temperature. After the reaction, SiO_2 nanospheres were centrifuged and washed by deionized water and ethanol for three times, respectively. Then, SiO_2 nanospheres were re-dispersed into 10 mL ethanol for further experiment.

2.3. Synthesis of TiO_2 hollow spheres

The monodisperse TiO_2 hollow spheres were prepared by using a modified silica-protected calcination method developed by Yin et al. In a typical synthesis, 1 mL SiO_2 nanosphere suspension was added into the mixed solution containing 10 mL ethanol and 7 mL acetonitrile. After ultrasonication for 30 min, the mixture containing 0.5 mL TBOT, 3 mL ethanol and 1 mL acetonitrile was rapidly injected into the aforementioned mixture under continuously stirring for 6 h at room temperature. The precipitate was centrifuged and washed with deionized water and ethanol for three times, respectively, re-dispersed into 10 mL H_2O , and followed by adding 0.2 g PVP under continuously stirring for 12 h. Subsequently, the suspension was centrifuged and re-dispersed into 20 mL ethanol to form the

mixed solution. Then, 5 mL H₂O, 1 mL NH₃·H₂O (28 wt%) and 1 mL TEOS was successively added into the aforementioned mixture. After continuously magnetic stirring for 6 h, the precipitate was centrifuged, washed and dried in a vacuum drying oven at 40 °C for 12 h. The obtained product was directly calcined in air at 900 °C for 2 h with a heating rate of 2.5 °C·min⁻¹ to give the double-shell SiO₂/TiO₂/SiO₂ nanospheres. After calcining, the obtained SiO₂/TiO₂/SiO₂ nanospheres were etched with 20 mL NaOH aqueous solution (1 mol·L⁻¹) at 90 °C for 4 h to produce porous TiO₂ hollow spheres.

2.4. Synthesis of hierarchical porous SnS₂/rGO/TiO₂ hollow spheres

The hierarchical porous SnS₂/rGO/TiO₂ hollow spheres were fabricated by the multi-step method. The few-layered graphene oxide (GO) nanosheets were firstly fabricated from graphite flakes by the ultrasonic-assisted Hummers' method reported in our previous work [2]. Secondly, 0.4 g obtained TiO₂ hollow spheres was dispersed into 1.6 mL APTES and 20 mL isopropanol under continuously magnetic stirring for 24 h. The white suspension was centrifuged and washed by deionized water and ethanol several times, then dried in a vacuum drying oven at 60 °C for 12 h. 0.0168 g surface-modified TiO₂ hollow spheres and 0.0739 g SnCl₄·5H₂O were dispersed into certain concentration of GO aqueous solution under continuously magnetic stirring for 3 h. Subsequently, 0.1939 g L-cysteine was dissolved in the mixed suspension. After magnetic stirring for 1 h, the mixture solution was moved into a Teflon-lined steel autoclave and heated at 180 °C for 2 h. After being cooled to room temperature naturally, the products were centrifuged and washed thoroughly with deionized water and ethanol for three times, and dried under vacuum at 60 °C for 12 h. The composites with different contents of GO nanosheets were prepared according to the same method. The GO/TiO₂ hollow spheres with 16.7 wt%, 12.5 wt%, 10 wt% and 2 wt% GO nanosheets loading were named as TG-1, TG-2, TG-3 and TG-4 composites, and the corresponding as-prepared hierarchical SnS₂/rGO/TiO₂ hollow spheres were denoted as TGS-1, TGS-2, TGS-3 and TGS-4 composites, respectively. For comparison, the binary SnS₂/TiO₂ hollow spheres with different molar ratios were also prepared by the similar procedure, except that GO nanosheets were omitted. And the as-prepared samples with molar ratios of Ti/Sn in 1:2, 1:1 and 2:1 were denoted as TS-1, TS-2 and TS-3 composites.

2.5. Characterization

The X-ray diffraction (XRD) patterns were carried out by a Lab X XRD-6100 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). Field-emission scanning electron microscope (FE-SEM, FEI Quanta F250, 200 KV) and transmission electron microscopy (TEM; JEOL, JEM-2100) coupled with X-ray energy dispersive spectrometer (EDS) analysis were performed to investigate the structure, size and morphology in the as-prepared samples. The surface states, chemical composition and energy level structure of photocatalysts were characterized

by an AXIS Supra X-ray photoelectron spectroscopy (XPS), which equipped with an ultraviolet photoelectron spectrometer (UPS). The specific surface area and pore size distribution measured with the BET analyzer (BELSORP-Max, Microtrac-BEL) were analyzed by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The optical property tests were performed with a UV-2600 UV-vis spectrophotometer (SHIMADZU), using BaSO₄ as the reference. A FLS980 fluorescence spectrophotometer (Edinburgh Instruments; $\lambda_{\text{ex}}=325$ nm) was used to record the photoluminescence (PL) spectra. Fourier transform infrared spectra (FT-IR) and Raman spectra were obtained by a Nicolet iS50 spectrophotometer (ThermoFisher) and a LabRAM HR800 laser Raman spectrometer (HORIBA; $\lambda_{\text{ex}}=633$ nm), respectively.

2.6. Photoelectrochemical and electrochemical measurements

The dates of transient photocurrent density, electrochemical impedance spectra (EIS) and Mott-Schottky plots were collected on a CHI 660D electrochemical workstation using a conventional three-electrode cell system. Typically, the working electrodes were prepared as follows: 3 mg of as-prepared photocatalysts were dispersed into the mixed solution, including: 1 mL ultrapure water, 0.5 mL isopropanol and 50 μ L perfluorosulfonic acid polymer (Nafion). Then 50 μ L of the resultant slurry was coated onto the surface of the cleaned glassy carbon electrode (effective area: 0.076 cm²) and dried at room temperature overnight to form uniform film electrodes. Under ambient temperature (25 °C), the transient photocurrent response was performed on the electrochemical analyzer under irradiation by a 300 W xenon lamp (≥ 420 nm), which positioned 10 cm far from the surface of the working electrode. Meanwhile, a platinum gauze electrode and a Ag/AgCl electrode were served as the counter electrode and reference electrode, respectively. 100 mL 1 M Na₂SO₄ aqueous solution in a quartz cell was used as the electrolyte solution. The electrochemical impedance spectra (EIS) were also performed in an electrolyte containing 1 M Na₂SO₄ aqueous solution at frequency range from 0.01 Hz to 100 kHz (AC voltage of 5 mV amplitude) under ambient temperature. Moreover, the Mott-Schottky plots of the as-prepared samples were measured in 0.5 mol·L⁻¹ of Na₂SO₄ electrolyte at a frequency of 1 kHz. The difference is that the saturated calomel electrode is chosen as the reference electrode. It should be noted that sunless conditions were ensured when EIS and Mott-Schottky experiments were carried out.

2.7. Photocatalytic activity measurement

The photocatalytic performance of the as-prepared photocatalysts was evaluated by photodegradation of 20 mg·L⁻¹ RhB aqueous solution and photoreduction of 100 mg·L⁻¹ K₂Cr₂O₇ aqueous solution under visible light irradiation, respectively. In general, 70 mg of the as-fabricated photocatalysts were suspended into a specially designed photochemical reactor, which containing 70 mL of the aforementioned organic dye or Cr(VI) aqueous solution. It should be noted that the photocatalytic

Cr(VI) photoreduction over different samples was carried out in the presence of tartaric acid (hole scavenger). Before light irradiation, the mixtures were magnetically stirred in the dark for 1 h to establish adsorption-desorption equilibrium between the photocatalysts and the corresponding pollutants. A 300 W Xe lamp (PLS-SXE300, Beijing perfectlight technology co. Ltd) equipped with a cut-off filter ($\lambda > 420$ nm) was used as light source. During the visible light irradiation, 3 mL of the suspension was taken out at the given time intervals and centrifuged to remove the photocatalyst. At last, the supernatant solution was analyzed by a UV-2600 UV-vis spectrophotometer (SHIMADZU) at the corresponding characteristic absorption peaks (RhB at 553 nm, Cr(VI) at 350 nm). The recycling tests over the photocatalysts were carried out as the similar methods. The free radical scavenge experiments procedure was the same as that under the visible light, except the presence of different scavengers.

3. Results and discussion

3.1. Morphological and structural characterization

The overall procedure for the synthesis of the hierarchical porous $\text{SnS}_2/\text{rGO}/\text{TiO}_2$ hollow spheres is shown in Scheme 1. Uniform SiO_2 nanospheres were selected as a hard template. First, the TiO_2 precursor was coated on the surface of the SiO_2 nanospheres in-situ in the presence of the surfactant polyvinyl pyrrolidone (PVP). Subsequently, a silica layer was applied on the external surface of the TiO_2 precursor. This modified “silica-protected calcination” process is a vital step for inducing the crystallization of the amorphous TiO_2 to the anatase phase while avoiding nanocrystal coalescence and further phase transition under the high temperature calcination conditions [26]. Transmission electron microscopy (TEM) images (Fig. S1) show that the thicknesses of the TiO_2 interlayer and the outermost SiO_2 shell in the obtained well-defined double-shelled $\text{SiO}_2/\text{TiO}_2/\text{SiO}_2$ microspheres were approximately 100 and 73 nm, respectively. The SiO_2 core and protective layer were removed simultaneously by alkali etching to give the porous TiO_2 hollow spheres. Scanning electron microscopy (SEM) (Fig. 1(a)) and TEM images (Figs. 1(b) and (c)) clearly reveal that the ob-

tained TiO_2 exhibited a monodisperse hollow spherical structure with diameters of 687–720 nm. The hollow structure was further confirmed by the broken shell observed in Fig. 1(a). Notably, the use of PVP and the protective layer were necessary in order to provide a porous structure and prevent the coalescence of the TiO_2 shells during synthesis. Subsequent surface modification of TiO_2 using aminopropyl triethoxysilane (APTES) was carried out to facilitate the coupling of the GO nanosheets (Fig. S2) on the positively charged TiO_2 surface via electrostatic interactions. Even when the loading amount of GO was reduced from 16.7 wt% to 2 wt%, SEM (Fig. S3 and Fig. 1(d)), TEM (Fig. 1(e)), and high resolution transmission electron microscopy (HRTEM) (Fig. 1(f)) images of the GO/TiO_2 composites clearly indicated that the surfaces of the TiO_2 shells were wrapped with ultrathin GO nanosheets, resulting a wrinkled, rough surface. The observed lattice fringe spacing of 0.243 nm corresponded to the (103) facet of anatase TiO_2 . Finally, hierarchical porous $\text{SnS}_2/\text{rGO}/\text{TiO}_2$ hollow spheres were obtained via the hydrothermal method. For comparison, binary $\text{SnS}_2/\text{TiO}_2$ composites were also synthesized using this method.

The structures of the as-prepared photocatalysts were probed using SEM and TEM. When a Ti/Sn molar ratio of 1:1 was used, an appropriate amount of SnS_2 nanosheets were anchored vertically on the surface of TiO_2 to form a binary $\text{SnS}_2/\text{TiO}_2$ hollow sphere heterojunction (denoted as TS-2; Figs. S4(c) and (d)). As shown in Figs. S4(a) and (b) (denoted as TS-1), and Figs. S4(e) and (f) (denoted as TS-3), further increasing or decreasing the molar ratio of Ti/Sn resulted in excessive or inadequate coating of SnS_2 nanosheets on the surface of the TiO_2 shells, respectively. After the introduction of GO, the as-prepared ternary $\text{SnS}_2/\text{rGO}/\text{TiO}_2$ composites with a 2 wt% GO loading (denoted as composite TGS-4; Figs. 2(a)–(c)) exhibited a spherical morphology similar to that of the TS-2 composite. Energy dispersive X-ray (EDX) elemental mapping images of the TGS-4 composite (Figs. 2(e)–(i)) confirmed that the TiO_2 hollow spheres were encapsulated by rGO nanosheets. Additionally, the elements S and Sn were both distributed uniformly over the surface of the rGO, indicating the construction of a well-defined hierarchical $\text{SnS}_2/\text{rGO}/\text{TiO}_2$ hollow sphere heterojunction.

The selected-area electron diffraction (SAED) patterns of both the TS-2 (inset in Fig. S5(a)) and TGS-4 (Fig. 2(j)) compo-

Scheme 1. Schematic illustration of the synthetic procedure of the hierarchical porous $\text{SnS}_2/\text{rGO}/\text{TiO}_2$ hollow spheres.

Fig. 1. SEM (a), TEM (b), and HRTEM (c) images of TiO_2 hollow spheres; SEM (d), TEM (e), and HRTEM (f) images (inset of (e) is the corresponding SAED pattern) of GO/TiO_2 composite (TG-4; 2 wt% GO loading).

Fig. 2. SnS₂/rGO/TiO₂ composite with 2 wt% GO loading (TGS-4 composite): (a,d) SEM and (b,c) TEM images. EDS elemental mapping images of a selected area: (e) Ti, (f) O, (g) C, (h) Sn, and (i) S. (j) Corresponding SAED pattern and (k) HRTEM image.

sites suggested that these composites exhibited a polycrystalline structure. The corresponding HRTEM images in Fig. 2(k) and Fig. S5(c) show lattice fringes with interplanar spacings of 0.352 and 0.590 nm, which correspond to the (101) plane of anatase TiO₂ (JCPDS no. 21-1272) and the (002) plane of hexagonal SnS₂ (JCPDS no. 21-1231), respectively. In contrast to the TS-2 composite, the TGS-4 composite clearly shows a structure in which the dual catalysts TiO₂ and SnS₂ are spatially separated by the few-layered rGO interlayer. The intimate contact at the material interfaces is beneficial in terms of providing charge transfer pathways to achieve the spatial separation and rapid transport of the photo-induced charge carriers during the photoredox reaction [27–29].

The crystalline features and surface chemical compositions of the as-obtained samples were characterized in further detail using X-ray diffraction (XRD) patterns and X-ray photoelectron spectroscopy (XPS). As shown in Fig. 3(a), the main diffraction peaks at 25.28°, 37.80°, 48.05°, and 62.69° were indexed to the (101), (004), (200), and (204) planes of anatase TiO₂ (JCPDS no. 21-1272), respectively. Only one diffraction peak at 54.32° was assigned to rutile TiO₂ (JCPDS no. 21-1276). This further confirmed that phase transition and agglomeration during high temperature calcination (900 °C) were effectively prevented via the modified “silica-protected calcination” strategy. Additionally, peaks characteristic of hexagonal SnS₂ crystals were located at 15.00°, 28.22°, 29.26°, 41.99°, 50.08°, and 52.55° (JCPDS no. 21-1231), respectively. The resulting TS-2 and TGS-4 composites demonstrated good crystallinity and purity, in agreement with the HR-TEM observations. The two characteristic peaks at 1332.6 and 1582.3 cm⁻¹ in the Raman spectra

(Fig. 3(b)) were assigned to the D and G bands of graphene [30,31]. The mean intensity ratio between the D and G bands (I_D/I_G) in the TGS-4 composite was 1.26, which was slightly larger than that of the GO/TiO₂ composite. Additionally, the weak 2D (2620 cm⁻¹) and 2G (2894 cm⁻¹) peaks further confirmed the few-layered structure of the graphene [32,33]. As can be seen from the FT-IR spectra in Fig. S6, the intensities of the peaks corresponding to oxygen-containing functional groups in the TGS-4 composite were obviously lower than in the GO/TiO₂ composite. These results not only demonstrated the partial conversion of GO into rGO, but also confirmed the existence of additional structural defects originating from the coupling between the rGO interlayer and the SnS₂/TiO₂ composite [34,35].

The survey XPS spectrum of the TGS-4 composite (Fig. 3(c)) clearly exhibited strong C 1s, O 1s, Ti 2p, S 2p, and Sn 3d signals, further confirming the existence of rGO, SnS₂, and TiO₂ in the composite. The peaks at binding energies of 284.8, 286.7, 287.8, and 288.9 eV in the C 1s XPS spectrum of GO (Fig. 3(d)) were highly consistent with C–C, C–O, C=O, and O–C=O groups, respectively. The disappearance of the C=O peak (287.8 eV) in the TGS-4 composite reflects the fact that GO was reduced to some extent by the removal of some of the oxygen-containing functional groups during the hydrothermal treatment [32,36]. The three peaks in the O 1s XPS spectrum of the TGS-4 composite (Fig. 3(e)) centered at 530.6, 531.9, and 533.4 eV were attributed to hydroxyl groups adsorbed on the surface of TiO₂ and the O–C=O and C=O species of rGO, respectively. However, the O 1s XPS spectrum of TiO₂ can be deconvoluted into four individual peaks located at 529.4, 530.5, 531.8, and 533.3 eV. The new peak centered at 529.4 eV was attributed to the lattice oxygen (Ti–O–Ti) of TiO₂ [32,37,38]. In the TGS-4 composite, the two prominent peaks centered at 459.2 and 464.9 eV in the high-resolution Ti 2p spectrum (Fig. 3(f)) were assigned as the Ti 2p_{3/2} and Ti 2p_{1/2} peaks of the Ti⁴⁺ of TiO₂, respectively. As shown in Fig. 3(g), the S 2p XPS spectrum can be fitted into four discernible peaks. The two spin-orbit doublets located at 161.8 and 162.9 eV were assigned as the S 2p_{3/2} and S 2p_{1/2} peaks of the S²⁻ of metal sulfide [31]. The second doublet at 163.5 and 164.6 eV corresponded to the S 2p_{3/2} and S 2p_{1/2} states of polysulfide, respectively [31,39]. The high-resolution XPS spectrum of Sn 3d can be resolved into two peaks centered at 486.9 and 495.3 eV, corresponding to Sn 3d_{5/2} and Sn 3d_{3/2}, respectively. Notably, the binding energies of O 1s and Ti 2p in the TGS-4 sample were shifted to slightly higher binding energies by 0.1 and 1.1 eV, respectively, compared with those of pure TiO₂. In contrast, negative binding energy shifts of approximately 0.4 and 0.7 eV relative to the pristine SnS₂ spectrum were observed for S 2p and Sn 3d in the TGS-4 sample, respectively. This behavior was attributed to the strong interactions at the interfaces between TiO₂/SnS₂ and the rGO interlayer. The XPS results further indicated that the resulting SnS₂/rGO/TiO₂ heterojunction provided charge transfer channels for the spatial separation and rapid migration of photo-induced excited charge carriers.

3.2. Photocatalytic activity and stability

Fig. 3. XRD patterns (a) and Raman spectra (b) of the as-prepared samples obtained using an excitation wavelength of 633 nm; XPS survey spectrum (c) and high-resolution XPS spectra of the C 1s (d), O 1s (e), Ti 2p (f), S 2p (g), and Sn 3d (h) core levels of the different samples.

The visible-light photodegradation of the model contaminant RhB over different samples was then investigated. Prior to light irradiation, the photocatalytic system was continuously stirred in the dark for 60 min to ensure the establishment of the adsorption-desorption equilibrium (Fig. S7). As shown in Fig. 4(a), almost no RhB photodegradation occurred over the pure TiO₂ due to the rapid recombination of the photo-induced charge carriers [36]. In contrast, the pristine SnS₂ demonstrated a 75.2% RhB removal rate under visible light irradiation for 140 min, which was significantly higher than that of the TS-2 composite (about 59.1%). The TGS-4 composite showed the highest photocatalytic removal rate of 90.7%. As the GO content of the composite was increased, the resulting SnS₂/rGO/TiO₂ composites showed decreased photocatalytic performance in the removal of RhB. This result indicated that the introduction of an optimal amount of rGO between TiO₂ and SnS₂ is beneficial to the separation of the photo-induced charge carriers. As shown in Fig. 4(b), 88.6% RhB removal was observed over the TGS-4 composite after six consecutive cycles, indicating its high stability.

The photocatalytic activities of the different samples were also assessed by the visible-light-driven photoreduction of Cr(VI) in the presence of tartaric acid (a hole scavenger). As illustrated in Fig. 4(c), a 100 mg·L⁻¹ K₂Cr₂O₇ aqueous solution maintained good stability both in the absence of the catalysts and in the presence of tartaric acid alone. Pure TiO₂ exhibited a 31.8% removal rate in Cr(VI) reduction due to the fact that the photo-generated holes accumulated in the VB of TiO₂ could be directly quenched by the hole scavenger tartaric acid. Thus, the presence of the hole scavenger prolonged the lifetime of the photo-induced charge carriers. After embedding the rGO interlayer, the optimized TGS-4 composite displayed the highest photocatalytic reduction performance, with a 97.1% removal rate; those of SnS₂ and the TS-2 composite were 90.1% and 85.2%, respectively. More interestingly, the photocatalytic reduction activity of the ternary SnS₂/rGO/TiO₂ heterojunction gradually increased with decreasing rGO content. According to the results of a cyclic experiment (Fig. 4(d)), the removal efficiency of Cr(VI) over the TGS-4 composite was as high as 91.78% after six runs, confirming the high stability of the ter-

Fig. 4. Plots of RhB degradation (a) and Cr(VI) reduction (c); Cycling experiment results for the degradation of RhB (b) and reduction of Cr(VI) (d) over the TGS-4 composite; Plots of RhB degradation (e) and Cr(VI) reduction (f) over the TGS-4 composite in the presence of different scavengers. ($C_{\text{RhB}} = 20 \text{ mg L}^{-1}$; $C_{\text{K}_2\text{Cr}_2\text{O}_7} = 100 \text{ mg L}^{-1}$).

nary SnS₂/rGO/TiO₂ heterojunction.

Furthermore, radical trapping experiments were carried out to identify the main active species involved in the photoredox reaction. Based on the photodegradation plots shown in Fig. 4(e), after 140 min of visible light irradiation, the photodegradation efficiencies of RhB were 87.1% and 90.7% in the presence of benzoquinone (BQ, a superoxide radical ($\text{O}_2^{\cdot-}$) scavenger) and in the absence of any scavenger, respectively. Only 73.9% and 71.3% of RhB were removed in the presence of ethylenediamine tetraacetic acid disodium salt (EDTA-2Na, a hole (h^+) scavenger) and isopropanol (IPA, a hydroxyl radical ($\cdot\text{OH}$) scavenger), respectively, at the same illumination time. This behavior suggests that photo-excited holes and $\cdot\text{OH}$ species are the dominant reactive species in the photodegradation reaction [40]. Similar inhibition phenomena were observed during the photocatalytic reduction of Cr(VI). As shown in Fig. 4(f), the concentration of Cr(VI) remained unchanged in the presence of potassium bromate (KBrO_3 , an electron (e^-) scavenger) and in the absence of any photocatalysts. However, the reduction ratio of Cr(VI) over the TGS-4 composite in the presence of tartaric acid (a h^+ scavenger) was approximately 97.1%, which was higher than in the control trial (52%, no scavenger). The greatly improved photocatalytic activity indicated that the photo-excited electrons played a dominant role in Cr(VI) photoreduction.

3.3. Nitrogen adsorption-desorption, optical and photoelectrochemical properties, ultraviolet photoelectron spectra, and Mott-Schottky plot analysis

Generally, the construction of hollow structural photocatalysts with a large specific surface area provides a greater num-

ber of active sites. As shown in Figs. 5(a) and (b), the N₂ adsorption-desorption isotherms of both the TiO₂ hollow sphere and TGS-4 samples can be classified as type IV hysteresis curves, indicating their mesoporous structure. The distinct slit-shaped hysteresis loops were assigned as typical type 3 hysteresis, indicating that the mesoporous structure originated from the accumulation of massive nanoparticles. The presence of large amounts of mesopores would facilitate the mass transfer process of the reactants during the photoredox reaction process [41]. Notably, the TGS-4 composite exhibited a Brunauer-Emmett-Teller (BET) specific surface area of $81.7 \text{ m}^2 \text{ g}^{-1}$, which was significantly lower than that of the pure TiO₂ hollow spheres ($208.3 \text{ m}^2 \text{ g}^{-1}$). The Barrett-Joyner-Halenda (BJH) pore sizes of the TGS-4 composite were mainly distributed in the 1.5–3 nm range (inset in Fig. 5(b)), which was narrower than that of pure TiO₂ (3–13 nm; inset in Fig. 5(a)). The decreased specific surface area and pore diameter of the TGS-4 composite were probably due to the wrapping of rGO and SnS₂ nanosheets on the surface of TiO₂. These results indicate that changes in the specific surface area and pore size distribution were not dominant factors responsible for the significantly enhanced photocatalytic activity of the as-prepared hierarchical porous SnS₂/rGO/TiO₂ hollow sphere heterojunctions.

As shown in the UV-vis diffuse reflection (DRS) spectra in Fig. 5(c), the pure TiO₂ displayed an optical absorption edge at 387 nm. In contrast, the pristine SnS₂ exhibited a wide absorption edge at 598.5 nm. The coupling between TiO₂ and SnS₂ led to slightly decreased light absorption. The absorption edge of the as-obtained TS-2 composite was determined to be about 575.5 nm. The light absorption edge of the TGS-4 composite was observed at 548.7 nm, which clearly represented a broadened light absorption range compared to that of TiO₂. This

Fig. 5. N₂ adsorption-desorption isotherms of TiO₂ (a) and the TGS-4 composite (b); (c) UV-vis DRS spectra; (d) PL spectra excited at 325 nm; Transient photocurrent responses (e) and Nyquist plots (f) for the as-synthesized samples. The insets in (a) and (b) are the corresponding pore-size distribution curves.

redshift of the optical absorption of TGS-4 composite is beneficial in terms of visible light utilization [41]. Furthermore, the band gap of the semiconductor can be estimated from the absorption edges [32,41]. The bandgap energy of SnS₂ was estimated to be 2.07 eV, which is slightly smaller than those of the TGS-4 composite (2.26 eV) and pure TiO₂ (3.2 eV), respectively. Although a smaller band gap means that electron-hole pairs can more easily be generated under light illumination, the TGS-4 composite exhibited a higher level of activity in Cr(VI) reduction and RhB degradation than pure SnS₂, indicating that the construction of a heterojunction at both sides of the rGO interlayer was beneficial to the rapid migration and spatial separation of the photo-generated carriers, and thus effectively improved the photocatalytic activity of the composite.

The improvement in charge carrier separation was evaluated using the photoluminescence (PL) spectra (Fig. 5(d)). Pure TiO₂ clearly exhibited stronger emission intensity than pristine SnS₂, suggesting that the photo-generated charge carrier separation was poorer in TiO₂. Interestingly, formation of the binary SnS₂/TiO₂ composite led to slightly decreased emission intensity compared with those of the single components. Upon the introduction of the rGO interlayer, the TGS-4 composite exhibited obviously reduced signal intensity, which suggested significantly accelerated dissociation of the photo-induced charge carriers at the interfaces between the rGO interlayer and the SnS₂/TiO₂ composite [42]. Additionally, the periodic on/off photocurrent response is a main indicator used to evaluate the recombination rate of photo-generated electron-hole pairs. As shown in Fig. 5(e), the transient photocurrent of the pristine TiO₂ was negligible. After loading an appropriate amount of SnS₂, the photocurrent density value of the TS-2 composite

reached 5.91 $\mu\text{A cm}^{-2}$. The introduction of an rGO interlayer between TiO₂ and SnS₂ significantly improved the transient photocurrent. The optimized TGS-4 composite displayed the highest photocurrent density value of 28.25 $\mu\text{A cm}^{-2}$, indicating that the rGO interlayer could effectively promote interfacial charge separation and transfer. Moreover, the excellent charge mobility in the TGS-4 composite was also verified from the electrochemical impedance spectra (EIS). As shown in Fig. 5(f), the TGS-4 composite displayed a smaller semicircle diameter than the pristine TiO₂ and SnS₂ or the TS-2 composite, implying that the presence of the rGO interlayer remarkably improved the interfacial charge-separation efficiency of the hierarchical porous SnS₂/rGO/TiO₂ hollow sphere heterojunctions.

Furthermore, the energy level structure, work functions (W_s), and corresponding Fermi levels (E_f) of the hybrid heterojunction were thoroughly investigated using ultraviolet photoelectron spectroscopy (UPS) and Mott-Schottky plots. As demonstrated in Figs. 6(a)–(d) and Fig. S8, all the ionization potentials [equivalent to the valence band energy (E_{VB})] of the samples were evaluated by subtracting the width of the He I UPS spectra from the excitation energy (21.22 eV) [43–45]. Based on the second electron cutoff edge (E_{cutoff}) positions and the valence-band onset (E_f) relative to the E_f , the W_s of TiO₂ and SnS₂ were calculated to be 4.01 and 4.65 eV vs. vacuum level (Vac), respectively; these values were smaller than that of the rGO interlayer (5.56 eV vs. Vac). In addition, the E_{VB} values of TiO₂ and SnS₂ were calculated to be –7.12 and –6.53 eV vs. Vac, respectively. By combining these results with the band gaps determined from the UV-vis DRS spectra, the conduction band (CB) positions (E_{CB}) of TiO₂ and SnS₂ were estimated to be –3.92 and –4.46 eV vs. Vac, respectively. From the

Fig. 6. (a–d) UPS spectra of the different samples; Mott-Schottky plots of TiO₂ (e) and SnS₂ (f) in 2 mol L⁻¹ Na₂SO₄ electrolytes.

Mott-Schottky plots, which exhibited positive slopes (Figs. 6(e) and (f)), the flat-band potentials (E_{fb}) of TiO₂ and SnS₂ were measured to be -0.72 and -0.18 V vs. the saturated calomel electrode (SCE), respectively [46,47]. As for n-type semiconductor, the bottom position of the CB is consistent with the E_{fb} [48–50]. Using the standard conversion factors that 0 V vs. SCE equals 0.241 V vs. the reversible hydrogen electrode (NHE) and 0 V vs. NHE equals -4.44 eV vs. Vac, the E_{CB} values of TiO₂ and SnS₂ were estimated to be -0.479 and +0.061 V vs. NHE using Mott-Schottky curves; these values correspond to -3.961 and -4.501 eV vs. Vac, respectively. The results of the Mott-Schottky curve analysis further confirmed the accuracy of the above UPS analysis.

3.4. Photocatalytic mechanism

Based on the calculated parameters of the energy-level structure (Table S1), the energy level alignments of the TS-2 and TGS-4 composites and the corresponding photo-induced charge carrier transmission route were proposed. Normally,

when SnS₂ is directly anchored on the surface of TiO₂, electrons should flow across the interface from TiO₂ to SnS₂ until their E_f reach the same level due to the higher W_s of SnS₂. As shown in Fig. 7(a), after achieving Fermi equilibrium, a space charge region is formed close to the SnS₂/TiO₂ interface, which leads to a built-in interfacial electric field directed from TiO₂ towards SnS₂. The induced built-in electric field would generate a different potential distribution at each point in the space charge region. The additional surface potential would cause upward band bending in TiO₂ and have the opposite effect in SnS₂. Under visible light irradiation, only SnS₂ would be photo-excited to produce photo-generated electrons and holes. The interfacial potential barrier induced by the band bending, as well as the smaller CB and VB potentials of SnS₂, would simultaneously impede the injection of the photo-excited electrons and holes from the CB and VB of SnS₂ into those of TiO₂, respectively. Thus, this strategy is not effective for decreasing the high efficiency recombination of photo-generated charge carriers on SnS₂. As a result, the binary SnS₂/TiO₂ composite displayed unsatisfactory photocatalytic activity compared to that of pure

Fig. 7. Schematic of the energy level alignment and corresponding charge transfer process in the TS-2 (a) and TGS-4 (b) composites during the photo-redox reactions.

SnS₂. Encouragingly, this was not the case when an rGO interlayer was inserted between the TiO₂ shell and the outermost SnS₂ layer. As shown in Fig. 7(b), in the ternary composite, the electrons would flow from TiO₂ and SnS₂ across the respective interfaces to the rGO interlayer until their E_f reached equilibrium due to the higher W_s of rGO. This behavior would favor the formation of dual built-in electric fields at the space charge regions close to the TiO₂/rGO and SnS₂/rGO interfaces; the direction of these fields would be from TiO₂ and SnS₂ towards rGO. Under the influence of the built-in electric fields, the different potential distribution at each point in the space charge region would increase the surface potential, resulting in upward band bending in both TiO₂ and SnS₂. Under visible light illumination, the interfacial potential barrier induced by the band bending and built-in electric fields would have a negative influence on photo-induced electron transfer, causing the photo-induced electrons to remain in the CB of the SnS₂. In contrast, the built-in electric field would facilitate photo-induced hole injection from the VB of SnS₂ into the rGO interlayer. Therefore, the rGO interlayer acted as a classic hole injection layer rather than an electron transfer mediator, which significantly facilitated the spatial separation and rapid migration of photo-induced charge carriers in the SnS₂.

During the RhB photodegradation process, the photosensitive RhB can easily be excited to RhB* [51,52]. The photo-excited electrons in the lowest unoccupied molecular orbital (LUMO) of RhB could spontaneously transfer to the CBs of both TiO₂ and SnS₂ due to the more positive LUMO potential of RhB (−3.08 eV vs. Vac). Notably, the dissolved oxygen could only be directly reduced to form •O₂[−] by the electrons accumulated on the CB of TiO₂, and not by those of SnS₂, because the CB potential of SnS₂ is more negative than that of TiO₂ (−3.92 eV vs. Vac) and the reduction potential of O₂/•O₂[−] (−4.45 eV vs. Vac). The generated •O₂[−] would mineralize the RhB* to form intermediate products or the ultimate products CO₂ and H₂O [53]. However, the results of the trapping experiments indicated that •O₂[−] was not the dominant active species. Meanwhile, the photo-induced holes accumulated on the rGO interlayer could be rapidly captured by H₂O to yield •OH radicals due to the more positive oxidation potential of −OH/•OH (−6.49 eV vs. Vac) compared to the VB potential of SnS₂. Undoubtedly, both the photo-induced holes and •OH have strong oxidation ability and can directly decompose the RhB molecules.

Similarly, the spatial separation and directional migration of the photo-induced electron-hole pairs between TiO₂/SnS₂ and the rGO interlayer are favorable for the photoreduction of Cr(VI) in the TGS-4 composites. Since the calculated CB potential of SnS₂ is more positive than that of Cr(VI)/Cr(III) (−5.01 eV vs. Vac) [54], photoreduction of Cr(VI) by the photo-generated electrons would be the dominant pathway. The photo-generated holes accumulated on the rGO interlayer could be quenched directly by the hole scavenger. In short, the inserted rGO interlayer can serve as an efficient hole-transport layer. The synergistic effects of the hierarchical hollow structure, matched band alignment, and built-in interfacial electric field resulted in beneficial effects on the light-harvesting efficiency, spatial charge separation, and directional charge transfer in the

ternary SnS₂/rGO/TiO₂ hollow sphere heterojunction, which were responsible for its high photocatalytic activity.

4. Conclusions

In summary, a novel modified “silica-protected calcination” method was adopted to prepare a hierarchical porous SnS₂/rGO/TiO₂ hollow sphere heterojunction. The optimized hybrid system with a 2 wt% rGO loading exhibited superior visible-light-driven photocatalytic performance and durability for RhB decomposition and Cr(VI) reduction compared to pure TiO₂, pure SnS₂, or a binary SnS₂/TiO₂ composite. The advantageous hierarchical porous hollow structure not only improved the light absorption capability, but also exposed more active sites. Most importantly, the rGO interlayer inserted between TiO₂ and SnS₂ was an efficient hole-transporting layer, which was beneficial to the spatial charge separation and directional transfer at the interface of the tandem heterojunction. This novel design strategy prolonged the lifetime of the photo-induced charge carriers, and should provide new pathways to enhance photocatalytic activity in wastewater treatment.

Conflict of interest

The authors declare no conflict of interest.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version.

References

- [1] L. Yang, J. Huang, L. Shi, L. Cao, H. Liu, Y. Liu, Y. Li, H. Song, Y. Jie, J. Ye, *Appl. Catal. B*, **2018**, 221, 670–680.
- [2] L. Han, Y.-L. Zhong, K. Lei, D. Mao, Y.-Z. Dong, G. Hong, Y.-T. Zhou, D. Fang, *J. Phys. Chem. C*, **2019**, 123, 2398–2409.
- [3] M.-H. Wu, L. Li, Y.-C. Xue, G. Xu, L. Tang, N. Liu, W.-Y. Huang, *Appl. Catal. B*, **2018**, 228, 103–112.
- [4] D. Cao, H. An, X. Yan, Y. Zhao, G. Yang, H. Mei, *Acta Phys.-Chim. Sin.*, **2020**, 36, 1901051.
- [5] X. Shi, Z. Lou, P. Zhang, M. Fujitsuka, T. Majima, *ACS Appl. Mater. Interfaces*, **2016**, 8, 31738–31745.
- [6] B. Sun, W. Zhou, H. Li, L. Ren, P. Qiao, W. Li, H. Fu, *Adv. Mater.*, **2018**, 30, e1804282.
- [7] P. Zhang, X. W. D. Lou, *Adv. Mater.*, **2019**, 31, e1900281.
- [8] M. Xiao, Z. Wang, M. Lyu, B. Luo, S. Wang, G. Liu, H. M. Cheng, L. Wang, *Adv. Mater.*, **2018**, e1801369.
- [9] Q. Sun, N. Wang, J. Yu, J. C. Yu, *Adv. Mater.*, **2018**, 30, e1804368.
- [10] S. Wang, B. Y. Guan, X. Wang, X. W. D. Lou, *J. Am. Chem. Soc.*, **2018**, 140, 15145–15148.
- [11] M. Xing, B. Qiu, M. Du, Q. Zhu, L. Wang, J. Zhang, *Adv. Funct. Mater.*, **2017**, 27, 1702624.
- [12] L. Ling, L. Liu, Y. Feng, J. Zhu, Z. Bian, *Chin. J. Catal.*, **2018**, 39, 639–645.
- [13] X. Chen, R. Shi, Q. Chen, Z. Zhang, W. Jiang, Y. Zhu, T. Zhang, *Nano Energy*, **2019**, 59, 644–650.
- [14] Y. Al Salka, L. I. Granone, W. Ramadan, A. Hakki, R. Dillert, D. W. Bahnemann, *Appl. Catal. B*, **2019**, 244, 1065–1095.

Graphical Abstract

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Accelerating directional charge separation via built-in interfacial electric fields originating from work-function differences

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The built-in interfacial electric fields originating from differences in the work-functions facilitate the directional migration of photo-induced holes from the VB of SnS₂ to the rGO hole injection interlayer, leading to efficient charge separation and high photocatalytic activity.

- [15] G. D. Gesesse, C. Li, E. Paineau, Y. Habibi, H. Remita, C. Colbeau-Justin, M. N. Ghazzal, *Chem. Mater.*, **2019**, 31, 4851–4863.
- [16] J. Pan, Z. Guan, J. Yang, Q. Li, *Chin. J. Catal.*, **2020**, 41, 200–208.
- [17] B. Srinivas, M. A. Pandit, K. Muralidharan, *ACS Omega*, **2019**, 4, 14970–14980.
- [18] X. Jiao, X. Li, X. Jin, Y. Sun, J. Xu, L. Liang, H. Ju, J. Zhu, Y. Pan, W. Yan, Y. Lin, Y. Xie, *J. Am. Chem. Soc.*, **2017**, 139, 18044–18051.
- [19] G. Li, R. Su, J. Rao, J. Wu, P. Rudolf, G. R. Blake, R. A. Groot, F. Besenbacher, T. T. M. Palstra, *J. Mater. Chem. A*, **2016**, 4, 209–216.
- [20] Z. Xie, H. L. Tan, X. Wen, Y. Suzuki, A. Iwase, A. Kudo, R. Amal, J. Scott, Y. H. Ng, *ACS Appl. Mater. Interfaces*, **2019**, 11, 23125–23134.
- [21] E. Jokar, Z. Y. Huang, S. Narra, C.-Y. Wang, V. Kattoor, C.-C. Chung, E. W.-G. Diau, *Adv. Energy Mater.*, **2018**, 8, 1701640.
- [22] J. Liu, Y. Xue, Y. Gao, D. Yu, M. Durstock, L. Dai, *Adv. Mater.*, **2012**, 24, 2228–33.
- [23] S. Ye, C. Ding, R. Chen, F. Fan, P. Fu, H. Yin, X. Wang, Z. Wang, P. Du, C. Li, *J. Am. Chem. Soc.*, **2018**, 140, 3250–3256.
- [24] L. Xu, W.-Q. Huang, L.-L. Wang, Z.-A. Tian, W. Hu, Y. Ma, X. Wang, A. Pan, G.-F. Huang, *Chem. Mater.*, **2015**, 27, 1612–1621.
- [25] D. Yang, L. Zhou, W. Yu, J. Zhang, C. Li, *Adv. Energy Mater.*, **2014**, 4, 1400591.
- [26] J. B. Joo, Q. Zhang, I. Lee, M. Dahl, F. Zaera, Y. Yin, *Adv. Funct. Mater.*, **2012**, 22, 166–174.
- [27] D. Zhou, Z. Cai, X. Lei, W. Tian, Y. Bi, Y. Jia, N. Han, T. Gao, Q. Zhang, Y. Kuang, J. Pan, X. Sun, X. Duan, *Adv. Energy Mater.*, **2018**, 8, 1701905.
- [28] C. Xue, H. Li, H. An, B. Yang, J. Wei, G. Yang, *ACS Catal.*, **2018**, 8, 1532–1545.
- [29] C. Xue, X. Yan, H. An, H. Li, J. Wei, G. Yang, *Appl. Catal. B*, **2018**, 222, 157–166.
- [30] W. Lu, D. Wang, L. Guo, Y. Jia, M. Ye, J. Huang, Z. Li, Y. Peng, W. Yuan, X. Chen, *Adv. Mater.*, **2015**, 27, 7986–7991.
- [31] M. Wang, L. Cai, Y. Wang, F. Zhou, K. Xu, X. Tao, Y. Chai, *J. Am. Chem. Soc.*, **2017**, 139, 4144–4151.
- [32] X. Liu, D. Chao, D. Su, S. Liu, L. Chen, C. Chi, J. Lin, Z. X. Shen, J. Zhao, L. Mai, Y. Li, *Nano Energy*, **2017**, 37, 108–117.
- [33] Y. Lei, C. Yang, J. Hou, F. Wang, S. Min, X. Ma, Z. Jin, J. Xu, G. Lu, K.-W. Huang, *Appl. Catal. B*, **2017**, 216, 59–69.
- [34] T. Wu, L. Zou, D. Han, F. Li, Q. Zhang, L. Niu, *Green Chem.*, **2014**, 16, 2142–2146.
- [35] Z. Xiong, Y. Luo, Y. Zhao, J. Zhang, C. Zheng, J. C. Wu, *Phys. Chem. Chem. Phys.*, **2016**, 18, 13186–95.
- [36] Q. Lang, Y. Chen, T. Huang, L. Yang, S. Zhong, L. Wu, J. Chen, S. Bai, *Appl. Catal. B*, **2018**, 220, 182–190.
- [37] Z. Yue, A. Liu, C. Zhang, J. Huang, M. Zhu, Y. Du, P. Yang, *Appl. Catal. B*, **2017**, 201, 202–210.
- [38] C. Liu, Y. Fu, J. Zhao, H. Wang, H. Huang, Y. Liu, Y. Dou, M. Shao, Z. Kang, *Chem. Eng. J.*, **2019**, 358, 134–142.
- [39] I. Shown, S. Samireddi, Y. C. Chang, R. Putikam, P. H. Chang, A. Sabbah, F. Y. Fu, W. F. Chen, C. I. Wu, T. Y. Yu, P. W. Chung, M. C. Lin, L. C. Chen, K. H. Chen, *Nat. Commun.*, **2018**, 9, 169.
- [40] C. Xue, T. Zhang, S. Ding, J. Wei, G. Yang, *ACS Appl. Mater. Interfaces*, **2017**, 9, 16091–16102.
- [41] Y. Chao, P. Zhou, N. Li, J. Lai, Y. Yang, Y. Zhang, Y. Tang, W. Yang, Y. Du, D. Su, Y. Tan, S. Guo, *Adv. Mater.*, **2019**, 31, e1807226.
- [42] W. Liu, L. Cao, W. Cheng, Y. Cao, X. Liu, W. Zhang, X. Mou, L. Jin, X. Zheng, W. Che, Q. Liu, T. Yao, S. Wei, *Angew. Chem. Int. Ed.*, **2017**, 56, 9312–9317.
- [43] C. Zhu, C. Liu, Y. Zhou, Y. Fu, S. Guo, H. Li, S. Zhao, H. Huang, Y. Liu, Z. Kang, *Appl. Catal. B*, **2017**, 216, 114–121.
- [44] J. Liu, Y. Liu, N. Liu, Y. Han, X. Zhang, H. Huang, Y. Lifshitz, S.-T. Lee, J. Zhong, Z. Kang, *Science*, **2015**, 347, 970–974.
- [45] J. Barbe, M. L. Tietze, M. Neophytou, B. Murali, E. Alarousu, A. E. Labban, M. Abulikemu, W. Yue, O. F. Mohammed, I. McCulloch, A. Amassian, S. Del Gobbo, *ACS Appl. Mater. Interfaces*, **2017**, 9,

- 11828–11836.
- [46] Z. Jiang, W. Wan, H. Li, S. Yuan, H. Zhao, P. K. Wong, *Adv. Mater.*, **2018**, 30, 1706108.
- [47] T. F. Yeh, C. Y. Teng, S. J. Chen, H. Teng, *Adv. Mater.*, **2014**, 26, 3297–303.
- [48] L. Pan, S. Wang, J. Xie, L. Wang, X. Zhang, J.-J. Zou, *Nano Energy*, **2016**, 28, 296–303.
- [49] W. Zhen, X. Ning, B. Yang, Y. Wu, Z. Li, G. Lu, *Appl. Catal. B*, **2018**, 221, 243–257.
- [50] K. Chang, X. Hai, H. Pang, H. Zhang, L. Shi, G. Liu, H. Liu, G. Zhao, M. Li, J. Ye, *Adv. Mater.*, **2016**, 28, 10033–10041.
- [51] C. Xue, X. Xu, G. Yang, S. Ding, *RSC Adv.*, **2015**, 5, 102228–102237.
- [52] C. Xue, X. Yan, S. Ding, G. Yang, *RSC Adv.*, **2016**, 6, 68653–68662.
- [53] J. Li, Y. Xie, Y. Zhong, Y. Hu, *J. Mater. Chem. A*, **2015**, 3, 5474–5481.
- [54] R. Liang, L. Shen, F. Jing, W. Wu, N. Qin, R. Lin, L. Wu, *Appl. Catal. B*, **2015**, 162, 245–251.

源于功函数差异的界面内建电场调控载流子定向分离的作用机制研究

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摘要: 近年来, 由有机污染物和重金属引起的水污染对人类健康、生态系统和社会可持续发展构成了严重威胁. 而光催化技术以其高效、低成本、节能、无二次污染等优点成为解决日益严重的环境污染问题的一个极具吸引力的策略. 众所周知, 宽光谱吸收、高效载流子分离和快速的表面反应动力学是高性能光催化剂所必备的基本条件. 而多孔TiO₂空心球具有以下结构优势: (1)成本低、无毒、氧化还原电位适中、物理化学性质稳定; (2)中空结构有利于入射光多重散射, 而且大表面积可以暴露更多的活性位点; (3)多孔结构有利于传质过程. 但是, 窄光谱吸收和低的光生载流子分离效率严重阻碍了空心结构TiO₂的实际应用. 因此, 通过耦合窄带隙半导体构建异质结光催化剂可以有效提高光吸收和促进光生电荷的分离. 窄带隙($E_g = 2.18\text{--}2.44\text{ eV}$)半导体材料SnS₂具有无毒、化学性质稳定、低成本和宽谱响应等诸多优点. 若将超薄SnS₂纳米片锚定生长多孔TiO₂空心球表面, 将对异质结的光催化性能产生显著的影响. 一方面, 分级结构的空心球具有高可见光捕获率; 另一方面, 超薄SnS₂纳米片具有更短的载流子扩散距离, 从而有效地抑制光生载流子在催化相内部复合. 然而, 由于其能带结构的限制, 二元TiO₂/SnS₂复合材料很容易形成嵌入I型异质结, 在很大程度上降低了光催化氧化还原能力. 此外, 在光催化剂表面聚集的光生电子和空穴容易发生随机性复合. 因此, 迫切需要通过引入界面驱动力来调节表面载流子的分离和转移. 众多研究表明, 通过化学功能化可以实现对还原氧化石墨烯(rGO)的能带结构、功函数、电导率、亲水性和光学性质的调控. 功能化的rGO可以作为优良的空穴提取材料, 在rGO两侧分别耦合不同能级结构的半导体光催化材料, 通过异质界面能级和功函数差异带来的界面内建电场, 精确调控光生载流子在界面间的空间分离和定向迁移.

基于上述分析, 本文通过改进的“硅保护煅烧”方法合成了分级多孔SnS₂/rGO/TiO₂空心球异质结光催化剂. 分级多孔空心球的结构优势不仅增强其光捕获能力, 而且为光氧化还原反应提供了丰富的活性位点. 特别是, 在TiO₂和SnS₂纳米薄片之间嵌入的rGO中间层可以作为空穴注入层. 由不同功函数导致的界面内建电场可以精确地调控光生空穴从SnS₂纳米薄片的价带向rGO空穴注入层定向迁移, 显著延长了光生载流子的寿命. 在可见光照射下, 负载2 wt% rGO的分级多孔SnS₂/rGO/TiO₂空心球异质结光催化剂对罗丹明B染料的降解率可达97.3%, 对Cr(VI)的还原效率可达97.09%. 此外, 经过六个周期的循环实验, 该异质结催化降解罗丹明B和还原Cr(VI)的效率没有明显降低, 表现出较好的光催化稳定性.

关键词: SnS₂/rGO/TiO₂; 空心球; 光催化剂; 空穴注入层; Cr(VI)还原

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