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Yannan Zhou,^{*a,b*} Ting Wen,^{*a,b*} Binbin Chang,^{*a,b*} Baocheng Yang,^{**a,b*} Yonggang Wang^{**c*}

Heterostructures consisted of two semiconductors have merited considerable attention in photocatalytic applications due to the synergistic effect in the complex redox processes. The incorporation of solid solutions into such architectures can further offer extra variability to control the bandgap. In this work, we report the fabrication of a series of core–shell $Cd_{0.2}Zn_{0.8}S@BiOX$ (X = Cl, Br, I) microspheres via a solvothermal route with enhanced photocatalytic performance under visible light irradiation. By optimizing the synthesis conditions, uniform and porous $Cd_{0.2}Zn_{0.8}S@BiOX$ microspheres were achieved and the products were characterized thoroughly by X-ray diffraction, scanning electron microscope, transmission electron microscope, photoluminescence, absorption measurements and the photo-degradation of RhB. Remarkably, the electric structures of $Cd_{0.2}Zn_{0.8}S@BiOX$ composites can be continuously tuned by varying the composition of BiOX to achieve the best catalytic performance under visible light irradiation. Finally, greatly enhanced visible-light-driven photocatalytic efficiency was observed in the optimized $Cd_{0.2}Zn_{0.8}S@BiOI$ composites than their single-component counterparts, which may attribute to the increased light absorption and the improved electron-hole separation. The photocatalytic mechanism has also been proposed based on the experimental evidences and the theoretical band positions of $Cd_{0.2}Zn_{0.8}S@BiOI$.

Introduction

Semiconductor photocatalysis, which shown great promise in photocatalytic degradation of pollutants and water splitting for hydrogen production, has attracted considerable attention due to the growing environmental and energy issues.^{1,2} Presently, many traditional photocatalysts (such as $TiO_2^{3,4}$, $ZnO^{5,6}$) have made great progress during the past three decades. Unfortunately, the photocatalytic activity of traditional photocatalysts is still restricted due to the recombination of photo induced electrons and holes and the poor solar energy utilization. Recently, a great deal of effort has been devoted to fabricate novel photocatalysts which can enhance the efficiency of the photocatalytic process and extend the light adsorption range, such as BiOX and Cd_{1-x}Zn_xS solid solution.^{2,7} Bismuth oxyhalide compounds BiOX(X = Cl, Br, and I) as novel ternary oxide semiconductors, have attracted widespread attention due their optical properties and promising industrial to

layer of $[Bi_2O_2]^{2^+}$ and two layers of halogen ions connected by internal static electric fields, which can facilitate the photogenerated electron–hole pairs separation.^{13,14} As a typical solid solution semiconductor of CdS and ZnS, ternary Cd_{1-x}Zn_xS has been intensively investigated due to the controllable band gap energy and band positions through adjusting the composition ratio of cadmium to zinc and the excellent visible-light-driven photocatalytic activity in water splitting and the decomposition of organic compounds.^{15–17} Although the photocatalytic properties of BiOX and Cd_{1-x}Zn_xS have been widely examined, it is still a change to further improve the stability and suppress the electron-hole pair recombination by design of novel coaxial core-shell and composite heterojunctional nanostructures.

applications.⁸⁻¹² All the BiOX compounds are tetragonal

matlockite structure with a layered structure composing of a

Materials with well-fined heterostructures often exhibit superior or new functional properties compared to their singlecomponent counterparts. To utilize visible light more efficiently and improve visible light photocatalytic activity of BiOX and Cd_{1-x}Zn_xS, a lot of coupled semiconductor systems, such as BiOCl/BiOL,18,19 BiOBr-g-C₃N₄²⁰ BiOX/TiO₂^{21,22} BiOX/ graphene,^{9,23,24} BiOBr-CdS,¹³ $Cd_{1-x}Zn_xS-ZnS$,²⁵ Cd_{1} $_{x}Zn_{x}S@ZnS$,²⁶ CNT/Cd_{1-x}Zn_xS,¹⁶ and RGO-Cd_{1-x}Zn_xS²⁷ have been studied. The successful fabrication of heterojunctional photocatalysts can endow the composite systems with increased visible light absorption and promotional photo activity. Nevertheless, because of the different band gaps and structural

^aInstitute of Nanostructured Functional Materials, Huanghe Science and Technology College, Zhengzhou, Henan 450006, China. ^bHenan Provincial Key Laboratory of Nano-composite and Applications,

Chengzhou 450006, Henan Province, China. Chengzhou 450006, Henan Province, China.

Nevada 89154, United States. E-mail: yyggwang@gmail.com (Y. Wang).

[†]Electronic Supplementary Information (ESI) available: SEM and TEM images of BiOX and CZS@BiOX; EDX results and PL spectra of CZS, BiOX and CZS@BiOX; Photocatalytic degradation of RhB on CZS and BiOX]. See DOI: 10.1039/x0xx00000x

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complexity between two semiconductors, it is still a standing challenge to fabricate highly active and stable hetero-structured catalysts with suite band gaps and structure.

In our previous studies, we have synthesized a series of mesoporous $Cd_{1-x}Zn_xS$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1) microspheres with high specific surface areas and tunable bandgap, and the optimal Cd_{0.2}Zn_{0.8}S microsphere presents the best H₂ production performance under visible light irradiation.¹⁷ However, unfavourable phase stability of these sulphides semiconductors is observed during the cycling test, and additional efforts should make to overcome such problem. In this work, we introduce a facile hydrothermal route for the fabrication of core-shell Cd_{0.2}Zn_{0.8}S@BiOX microspheres with improved photocatalytic activity and phase stability under visible light irradiation. Though coating with BiOX on the surface, the photo response range of $Cd_{0.2}Zn_{0.8}S$ microspheres are successfully extended into the visible region. The intimate contact and chemical potential difference in the core-shell microstructure could effectively facilitate the transfer efficiency and suppress there combination rate of photo-excited carriers, resulting in extremely high activity and stability. The photocatalytic efficiency and stability of Cd_{0.2}Zn_{0.8}S@BiOX are investigated in terms of the degradation of Rhodamin B (RhB), which exhibits superior photocatalytic performance compared with the pure BiOX and Cd_{0.2}Zn_{0.8}S, indicating their potential applications for visible-light-driven catalyses. The possible photocatalytic mechanism has also been proposed based on the relative experiments and band positions of the two semiconductors.

Experimental

Synthesis of Cd_{0.2}Zn_{0.8}S microspheres. Cd_{0.2}Zn_{0.8}S microspheres were prepared following the strategy reported in our previous work.¹⁷ In a typical synthesis procedure (for the Cd^{2+} : $Zn^{2+} = 1$: 4 sample), stoichiometric $Cd(NO_3)_2 \cdot 4H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ were dissolved in 50 vol.% diethylenetriamine (DETA) aqueous solution, the total amount of Cd(NO₃)₂·4H₂O and Zn(NO₃)₂·6H₂O was 2 mmol. After constant stirring for 15 min at room temperature, 2 mmol cysteine (Cys) was slowly added with stirring for another 15 min. Cd_{0.2}Zn_{0.8}S microsphere could be obtained after the autoclave was heated at 180 °C for 24 h and then cooled down to room temperature. The asprepared Cd_{0.2}Zn_{0.8}S microspheres were denoted as CZS hereafter.

Synthesis of BiOX. In a typical synthesis, 2 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 10 mL ethylene glycol (EG), then the stoichiometric amount of KX (X = CI, Br, I) was slowly added with the Bi/X molar ratio of 1. The mixture was stirred for 30 min at room temperature, and then poured into a 40 mL Teflon-lined stainless autoclave until 50% of the autoclave volume was filled. The autoclave was allowed to be heated at 160 °C for 12 h, and then cooled down to room temperature naturally. The resulting samples were centrifuged and washed with deionized water and ethanol thoroughly and dried at 60 °C overnight.

Synthesis of Cd_{0.2}Zn_{0.8}S@BiOX core@shell microspheres. In a typical synthesis, the CZS microspheres were dispersed in 10 mL ethanol solution firstly. Then 0.5 mmol Bi(NO₃)₃·5H₂O and 0.5 mmol KX (X = Cl, Br, I) were dissolved in 10 mL ethylene glycol (EG) and the as-obtained solution was dropped slowly into the above-mentioned CZS ethanol solution. After stirred at room temperature for 30 min, the resulting mixture was transferred into a Teflon-lined stainless steel autoclave of 40mL capacity. The autoclave was sealed and maintained at 160 °C for 12 h and then cooled to room temperature naturally. The resulting samples were centrifuged and dried in an oven at 80 °C overnight and the products are denoted as CZS@BiOX(X = Cl, Br, I). The samples with various CZS/Bi(NO₃)₃·5H₂O weight ratios of 1:1, 1:2.5, and 1:5 were prepared in the same way. The resulting composite is denoted as x:y CZS@BiOX, where x: v is the weight ratio of CZS to $Bi(NO_3)_3 \cdot 5H_2O$.

Characterization. The powder X-ray diffraction (XRD) patterns of all the samples were collected at room temperature on a Bruker D8 Advance diffractometer using a germanium monochromatic (Cu-Ka radiation, 40 kV and 40 mA). The data for phase identification were taken in the 2 theta range between 10° and 70° and with the remaining time of 0.1 s/step. Scanning electron microscope (SEM) images were recorded using a Quanta 250 FEG FEI at 20 kV in gentle-beam mode without any metal coating. Transmission electron microscope (TEM) images were recorded on a Tecnai G2 20 TEM with an accelerating voltage of 200 kV using a carbon-coated copper grid. The textural properties were studied by N2 adsorptiondesorption measurements (ASAP2020, America) at liquid nitrogen temperature. Before analysis, the samples were degassed in vacuum at 180 °C for 6 h. UV-vis diffuse reflectance spectra (DRS) were measured by using a U-4100 UV-Vis-NIR spectrometer (Hitachi). Photoluminescence (PL) spectra were collected on a Varian Cary Eclipse fluorescence spectrophotometer at room temperature with either a 550 nm laser beam or a 300 W Xe-lamp as the light sources.

Photocatalytic activity tests. Photocatalytic activity of the asprepared core–shell CZS@BiOX microspheres were evaluated by photo-degradation of RhB using a 200 mL quartz reactor under irradiation of a 300 W Xe lamp (CEL-HXF300) with a 420 nm cut-off filter. A recycling water pump was used to keep the reactor temperature constant at 10 °C. The photocatalyst (1 g/L) was dispersed into 100 mL RhB solution (20 mg/L). Prior to irradiation, a mixture with photocatalyst were stirred for 30 min in darkness in order to reach the adsorption–desorption equilibrium. 3 mL suspension was collected and centrifuged at regular intervals to measure the UV-visible absorption spectrum by using a spectrophotometer (Hitachi, U-4100). To investigate the stability of catalysts, the specimen after one trial was washed and dried for the subsequent recycling test.

Active species trapping experiments. To detecting the active species during photocatalytic process, 1.0 mM isopropanol (IPA), 1.0 mM benzoquinone (BQ) and ammonium oxalate (AO) were added into the RhB solution as •OH quencher, $•O_2^-$ quencher and h⁺ quencher, respectively.

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RESULTS and DISCUSSION

Characterizations of core-shell CZS@BiOX microspheres. To date, a variety of strategies have been employed to synthesis efficient visible-light photocatalytic materials. Among these approaches, formation of core-shell structured nanocomposites/ microcomposites is considered to be a facile method to improve the photo-induced charges separation efficiency and the photochemical activity, and has been extensively studied for the last decades.^{7,28,29} Semiconductor core-shell composites which often display superior physical and chemical properties over their single-component counterparts³⁰ can be divided into three different cases: type-I, type-II and type-III band alignment depending on the bandgaps and the electronic affinity of semiconductors. Taking the type-II band alignment for example, the position of valance and conduction bands of the core semiconductor is higher than that of the shell semiconductor. The chemical potential difference causes band bending at the interface of junction, which can induce a built-in field to accelerate the spatial separation of the electron-hole pairs on different sides of the core-shell composites.^{7,31} In our experiments, type II core-shell CZS@BiOX microspheres were achieved via a two-step solvothermal method. The pristine BiOX microspheres present hierarchical superstructures built up of irregular nanoplates, and the sizes of these spheres are 1~2 μ m which are consistent with the previous reports (Fig. S1).^{8,14} The SEM images of the CZS@BiOX core-shell microspheres as well as the as-prepared CZS microspheres are depicted in Fig. 1. The SEM images reveal that the pure CZS appears as separate microspheres with diameters of 1~2 µm and the distinct core-shell microstructure demonstrates the successful coating of BiOX shells on the CZS cores. To further elucidate their microstructure, EDX elemental technique was applied to the CZS@BiOX composites. Fig. S2 presents that the elements including Bi, S, Cl/Br/I and O coexist in the CZS@BiOX hybrid, which further confirms the successful formation of CZS@BiOX composites.

Previous investigations have demonstrated that the shelllayer thickness which directly influences their performance can be controlled by simply changing the content of raw materials.7,29 The TEM images reveal that pure CZS is composed of irregular nano-sized blocks with an average diameter of ~1-2 μ m (Fig. 2). BiOX (X = Cl, Br, I) powders are composed of nanosheets aggregated together and selfassembled into urchin-like spheres (Fig. S3). The TEM images of the core-shell microcomposites CZS@BiOX with different mass ratios of CZS to Bi(NO₃)₃·5H₂O ranged from 1:1 to 1:5 are shown in Fig. 2 and Fig. S4. It was also found that wellshaped core-shell CZS@BiOX microspheres could be obtained in the whole examined ranges. In the case of 1:1 CZS@BiOX, the formations of shell layers were incomplete due to the low content of BiOX. With regard to the 1:1.25 CZS@BiOX, it shows a core-shell structure with lumpy BiOX flakes covered on the CZS microspheres core. As the CZS/Bi(NO₃)₃·5H₂O mass ratio increased to 1:5, there was a dramatic density increase of BiOX shells in the achieved products, resulting in the cotton-like coatings encircled each microspheres. In the present work, the 1:2.5 weight ratio of CZS to $Bi(NO_3)_3$ ·5H₂O was used for all the samples mentioned in this article.



Fig. 1 The low-magnification SEM images of CZS (a), CZS@BiOC1 (b), CZS@BiOBr (c) and CZS@BiOI (d). Scale bar: 5 $\mu m.$



Fig. 2 TEM images of CZS (a), CZS@BiOCl (b), CZS@BiOBr (c) and CZS@BiOI (d). Scale bar: 500 nm.

Fig. 3 describes the XRD patterns of BiO*X*, CZS and the corresponding CZS@BiO*X* composites (X = Cl, Br, I). The XRD patterns of pure BiO*X* agree well with the tetragonal structures of BiOCl (JCPDS #73-2060), BiOBr (JCPDS #73-2061), and BiOI (JCPDS #73-2062), respectively. The coreshell structured CZS@BiO*X* microspheres demonstrate an obviously coexistence of both CZS and BiO*X* phases with no other impurity phases from the diffraction patterns, indicating that there are no appreciable chemical reactions between CZS and BiO*X*. The diffraction patterns of CZS@BiO*X* and the hexagonal CZS.

The optical response of samples in the visible region is systematically evaluated by UV-vis DRS (**Fig. 4**). The transmittance cut-off edge of pure CZS is determined to be 490 nm, corresponding to bandgap energy of 2.55 eV. While, for BiOCl, BiOBr and BiOI, the bandgap values are derived to be 3.12, 2.58 and 1.92 eV, respectively. The derived bandgap values of CZS and BiOX could calculate by Kubelka-Munk (KM) method, $\alpha hv = A(hv-E_g)^{n/2}$, where α and E_g are the absorption coefficient and bandgap energy, CZS (n = 1) and BiOX (n = 4) pertain to direct and indirect transitions, respectively. The calculated bandgaps are provided in **Table 1**. From these observed interactions between bare CZS and BiOX counterparts, we can say that the hetero-structured CZS@BiOX

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core-shell photocatalysts are successfully fabricated. Surprisingly, all the CZS@BiOX composites are black in color after the formation processes of the core-shell heterojunction, which are consistent with the high background of the absorption in the visible light range up to 800 nm. We tentatively attribute this phenomenon to the oxygen and sulfur defects on the surface of the products, similar as those reported in the previous studies.^{32–34}



Fig. 3 Powder XRD patterns of (a) BiOX (X = Cl, Br, I) and (b) CZS CZS@BiOX (X = Cl, Br, I).



Fig. 4 (a) UV-vis DRS of CZS, BiO*X* and CZS@BiO*X* (X = Cl, Br, I). (b) Band gaps of CZS and BiO*X* established from the absorption data.

The photocatalytic activity can be significantly inhibited by the recombination of photo-induced electron-hole pairs. PL spectra can be used as a useful strategy to evaluate the recombination efficiency in a semiconductor photocatalyst.³⁵⁻³⁹ Firstly, we focused on the visible light region around the CZS emission bands (580-680 nm). The PL spectra of as-obtained CZS, BiOX and CZS@BiOX excited at 550 nm are presented in **Fig. S5**. The emission intensity of the as-prepared CZS@BiOX decreases in the order of CZS@BiOI < CZS@BiOBr < CZS@BiOCI. These two bands become imperceptible for the CZS@BiOI microspheres. Since the PL intensity is proportional to the recombination rate of the photo-induced electrons and holes, the constructing of the core-shell architecture do suppress the recombination of photo-induced electron-hole pairs effectively.

Fig. 5 depicted the N₂ adsorption-desorption isotherms and pore size distributions of all as-obtained samples. All materials showed a slope of isotherm with a clear hysteresis loop at relative pressure from 0.5 to 1.0, indicating the porosity was mainly composed of mesopores. Apparently, all isotherms presented a sharp capillary condensation step at the high relative pressure, implying the existence of mesopores with a relatively large pore size or even marcopores. For the CZS@BiOX samples (especially when X = I), the curve sloop and the hysteresis loop increased gradually, indicating the formation of more slit-shaped mesopores and active sites on the surface. More interestingly, CZS@BiOX composites exhibited a closed surface area with BiOX samples (**Table 1**), which should be ascribed to the complete coating of BiOX on CZS microspheres. The insert displayed the pore size distribution of as-made samples. For BiOX samples, the pore size mainly centered at ca. 2.0 and 2.7 nm. Notably, benefiting from their mesoporous heterostructures, CZS@BiOX core-shell spheres exhibited an extra larger pore distribution centered around 12 nm besides the original pores centered around 2.7 nm, which may greatly improve the reactants transmission efficiency and the utilization of active sites on the surface.^{40,41}



Fig. 5 Nitrogen adsorption-desorption isotherms of the CZS, BiOX, CZS@BiOX (X = Cl, Br, l). Inset shows the derived pore-size distribution curves.

Photocatalytic activity and stability. The photocatalytic activities of core-shell CZS@BiOX microspheres were evaluated by the degradation of RhB under visible light irradiation in aqueous solution (420 nm $\leq \lambda \leq$ 780 nm). As a model pollutant to evaluate the photocatalytic activity of a given catalyst, the decomposition mechanism of RhB has been well-characterized⁴²⁻⁴⁴ to go through a stepwise chromophore cleavage process, redox reactions to terephthalic and benzoic acids etc., and finally into CO₂ and H₂O (Fig. S6). During the process, the concentration of RhB can be easily detected by the intensity decrease of the emission peak around 550 nm. Fig. 6a and Fig. 6b present the concentration of RhB as a function of irradiation time over CZS and CZS@BiOI catalysts. The continual fading of the coloration of RhB solutions obviously illustrates a steady and continuous degradation of the organic dyes. The absorption peak at 554 nm decreases gradually as the irradiation time increased, which demonstrates the destruction of the conjugated structure due to the incomplete mineralization of RhB during the visible light irradiation. The curve plotted for BiOCl and BiOBr shows the minute photocatalytic activity under visible light due to the wide band gap (Fig. S6). After CZS coating on the BiOX particles, the core-shell hybrid catalyst displays enhanced photocatalytic performance, and CZS@BiOI composite exhibits the highest photocatalytic activity for the degradation of RhB. As for the individual BiOI and CZS, the photocatalytic efficiency on RhB are 50% and 71%, respectively (Fig. S6). While, almost 98% of RhB is degraded over CZS@BiOI after irradiation for 120 min under Published on 28 July 2016. Downloaded by Northern Illinois University on 30/07/2016 12:55:11

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visible light. The kinetics of RhB degradation is revealed by applying the pseudo-first-order model and the results are listed in **Table 1**.



Fig. 6 Absorption spectra of RhB aqueous solution in the presence of the CZS (a) and CZS@BiOI (b). Photocatalytic degradation of RhB on blank and CZS@BiOX (X = CI, Br, I) under visible-light irradiation (c). Cycling performance for the photocatalytic degradation of RhB over CZS and CZS@BiOI under visible light irradiation (d).

Table 1. Summarized CB, VB potentials and catalysis-related properties of CZS, BiOX and CZS@BiOX (X = Cl, Br, I).

Material	$S_{BET} (m^2/g)$	E _g , eV	E_{CB} , eV	E_{VB}, eV	$K(\min^{-1})$
CZS	98.09	2.55	-0.53	2.02	0.008
BiOCl	30.35	3.12	0.59	3.71	0.002
BiOBr	43.82	2.56	0.67	3.23	0.002
BiOI	70.15	1.92	0.75	2.67	0.004
CZS@BiOCl	44.42				0.007
CZS@BiOBr	45.18				0.013
CZS@BiOI	64.51				0.018

It was reported that the synthesis method could affect the morphology, size and surface area of the photocatalysts, and thus decide the adsorption behavior and photocatalytic activity of $BiOX^{45}$ To compare the features of the materials via different synthetic routes, we provide a brief summary of our as-fabricated BiOX (X = Cl, Br, I) photocatalysts together with those reported previously in Table S1. We speculate that different synthetic routes may lead to distinct pollutant adsorption and light absorption behavior, and thus diverse photocatalytic performance under visible light. The kinetic reaction rate constants k values of core-shell hybrid catalysts are 0.007 min⁻¹ (CZS@BiOCl), 0.013 min⁻¹ (CZS@BiOBr) and 0.018 min⁻¹ (CZS@BiOI), respectively. The enhanced catalytic activity of CZS@BiOI can be attributed to the raised light absorption capability and the improved separation and transfer efficiency of photo-generated electron-hole pairs. Fig. 6d depicts the cycling runs for the photocatalytic degradation of RhB over CZS and CZS@BiOI under visible-light irradiation. No obvious decay of the photo-degradation efficiency was observed after five circulatory experiments, suggesting that the

as-obtained photocatalysts are stable enough during the photocatalytic process. The enhanced stability and durability of CZS@BiOI can be attributed to the following two reasons: 1) The accelerated separation of photo-generated electron-hole pairs due to the effective heterojunction between the CZS and BiOI, which reduce the opportunity of the undesirable oxidization of S²⁻ ions; 2) BiOX layers in the core-shell architecture can protect the inside CZS cores from aggregation during the photo-degradation processes.

Photocatalytic mechanism of core-shell CZS@BiOX microspheres. As discussed above, the superior photocatalytic activity and stability of the core-shell CZS@BiOX microspheres were attributed to the efficient separation and fast transfer of photo-generated charges at the interface of core-shell micro-architectures. To investigate the detailed photocatalytic mechanism of CZS and CZS@BiOI core-shell microspheres, radicals trapping experiments were conducted to estimate the role of different reactive species by adding various scavengers in the photocatalytic degradation of RhB. BQ, AO and IPA were used to trap the $\bullet O_2^-$, h^+ and $\bullet OH$ radicals, respectively.^{12,18,46} As shown in Fig. 7, the degradation efficiency of RhB over CZS and CZS@BiOI is significantly inhibited by adding AO and BQ scavengers, implying that the h^+ and $\cdot O_2^-$ radicals plays major roles in the catalytic processes. Comparatively, the addition of IPA shows weaker influence on the photocatalytic oxidation process of RhB over CZS and CZS@BiOI, indicating the less participation of •OH radicals during the photo-degradation process. These evidences clearly demonstrate that the h^+ and $\cdot O_2^-$ radicals play more important roles than that of •OH in the photo-degradation process of RhB over CZS and CZS@BiOI catalysts.



Fig. 7 The impact of reactive species in the photo-degradation process of RhB over CZS (a) and CZS@BiOI (b). Scavengers used in the experiments: Blue, None; Green, 1.0 mM IPA; Cyan, 1.0 mM AO; Purple, 1.0 mM BQ.

To further evaluate the •OH radicals produced in the catalytic process, PL signals with terephthalic acid (TA) as the probe was collected, since TA was believed that could react with •OH radicals readily to produce 2-hydroxyterephthalic acid with highly fluorescent emissions.^{18,47,48} The PL spectra from NaOH solution of TA (excitation at 315 nm) over CZS and CZS@BiOI are shown in **Fig. 8**. Significant PL signal centered at ca. 415 nm is observed during the photocatalytic process, which confirms the production of •OH radical during the photocatalytic process. Nevertheless, the PL intensities for CZS@BiOI photocatalyst are much weaker than that of CZS photocatalyst, which indicates that the emerging hydroxyl radical is not the main oxygen species in the degradation process of RhB.



Fig. 8 The PL spectra of TA over the CZS (a) and CZS@BiOI microspheres (b) excited at 315 nm in NaOH solution.



Fig. 9 Schematic illustration of the formation of CZS@BiOX microspheres and photocatalytic processes of CZS@BiOI under visible-light irradiation.

In order to understand the photocatalytic mechanism, CB and VB positions of CZS and BiOX were calculated based on the experimental data and empirical equations. The results are shown in **Table 1**. Taking BiOI as example, band edge positions are given by the following equations:^{49,50}

$$E_{c} = (\chi_{(\text{Bi})} \cdot \chi_{(\text{O})} \cdot \chi_{(\text{I})})^{1/(3)} - 1/2 E_{g} + E_{0}$$
(1)
$$E_{v} = E_{c} + E_{g}$$
(2)

The absolute electro-negativities of the constituent atoms Bi, O, and I are $\chi_{(Bi)} = 4.69$, $\chi_{(O)} = 7.54$, and $\chi_{(I)} = 6.76$, respectively.50 E_C , E_V , and E_g are the energy levels of the CBM, VBM and the bandgap energy of the semiconductor respectively. Eg were determined by the UV-vis DRS, and $E_0 = -4.5 \text{ eV}_{VAS}$ at pH = 0. Based on these results, we provided the schematic illustration of fabrication CZS@BiOX microspheres and photocatalytic mechanism scheme of CZS@BiOI under visible-light irradiation in Fig. 9. When the CZS@BiOI microsphere is exposed to visible light, both semiconductors are activated. As for CZS@BiOI, the redox potential of both CB and VB ($E_{CB} = -$ 0.53 eV, E_{VB} = +2.02 eV) of CZS are more negative than those of BiOI ($E_{CB} = 0.75 \text{ eV}$, $E_{VB} = +2.67 \text{ eV}$). The band potential overlapping between CZS and BiOI semiconductors suggests that the combination of these two materials can form an effective heterojunction. Since the CB potential of CZS is more negative than the CB edge of BiOI, electrons will transfer from CZS to BiOI and the holes generated in the VB of BiOI will migrate to the VB of CZS spontaneously. The charge carriers are successfully separated between the CZS core and the BiOI shell, thus more effective electrons and holes are taking account into the photo-degradation process. The electrons in the CB of BiOI shell then react with O2 adsorbed on the surface of the

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composite to produce $\cdot O_2^{-}(O_2^{-}) = -0.046 \text{ eV}^{51}$ and then decompose RhB. Nevertheless, the VB of CZS (2.02 eV) is less positive than the standard reduction potential of •OH/OH⁻ (1.99 eV),⁵² suggesting that the h^+ on the surface of CZS cannot oxidize OH into •OH radicals, the main source of the •OH radicals in the detection experiment may produce by the $\cdot O_2^{-1}$ reducing H₂O into •OH radicals. The photo-degradation activity of RhB declined marginally when IPA was added, therefore the RhB photo-degradation of CZS@BiOI composites may be initiated by the direct surface hole and electron transfer rather than the oxidation by •OH. Furthermore, one should be aware that the overall photocatalytic performance of a given material relied on the cooperation of the pollutant adsorption, light harvesting, and efficient separation of photo-induced charge carrier. Therefore, the enhanced catalytic performance of the optimized CZS@BiOI hetero-structures can be attributed to the improved visible light absorption, and the accelerated separation of photo-generated electron-hole pairs.

Conclusions

In conclusion, we report a facile method to fabricate a family of core-shell Cd_{0.2}Zn_{0.8}S@BiOX microspheres by coating BiOX (X = Cl, Br, I) onto $Cd_{0.2}Zn_{0.8}S$ microspheres. The Cd_{0.2}Zn_{0.8}S@BiOX microspheres exhibit enhanced photocatalytic activities and stability toward visible-lightdriven degradation of RhB compared to their single-component counterparts. The excellent photocatalytic performance of the products can be attributed to the synergistic effect derived from the well-fined hetero-structures between $Cd_{0.2}Zn_{0.8}S$ and BiOX, which can improve the light absorption and accelerate the separation of the photo-generated electrons and holes. Our work develops a simple preparation route to obtain semiconductor composites for various energy and environmentrelated applications.

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Notes and references

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- X. Chen, S. Shen, L. J. Guo and S. S. Mao, *Chem. Rev.*, 2010, **110**, 6503–6570.
- R. Abe, J. Photochem. Photobio. C, 2010, 11, 179-209.
- X. Chen and S. S. Mao, *Chem. Rev.*, 2007, **107**, 2891–2959.
- U. I. Gaya and A. H. Abdullah, *J. Photoch. Photobio. C*, 2008, **9**, 1–12.
- S. Rehman, R. Ullah, M. Butt and N. D. Gohar, J. Hazard Mater., 2009, 170, 560–569.
- K. Maeda and K. Domen, *Chem. Mater.*, 2010, **22**, 612–623.
- Y. Wang, Q. Wang, X. Zhan, F. Wang, M. Safdar and J. He, *Nanoscale*, 2013, **5**, 8326–8339.
- H. Cheng, B. Huang and Y. Dai, *Nanoscale*, 2014, **6**, 2009-2026.

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Journal Name

- 9 H. Liu, W. Cao, Y. Su, Z. Chen and Y. Wang, J. Colloid Interf. Sci., 2013, 398, 161–167.
- 10 X. Zhang, Z. Ai, F. Jia and L. Zhang, *J. Phys. Chem. C*, 2008, **112**, 747–753.
- 11 H. Li, J. Liu, X. Liang, W. Hou and X. Tao, *J. Mater. Chem. A*, 2014, **2**, 8926–8932.
- 12 L. Ye, J. Liu, C. Gong, L. Tian, T. Peng and L. Zan, *ACS Cata.*, 2012, **2**, 1677–1683.
- 13 Y. Guo, H. Huang, Y. He, N. Tian, T. Zhang, P. K. Chu, Q. An, Y. Zhang, *Nanoscale*, 2015, **7**, 11702–11711.
- 14 Z. Jiang, B. Huang, Z. Lou, Z. Wang, X. Meng, Y. Liu, X. Qin, X. Zhang and Y. Dai, *Dalton Trans.*, 2014, **43**, 8170– 8173.
- 15 Q. Li, H. Meng, P. Zhou, Y. Zheng, J. Wang, J. Yu, *ACS Cata.*, 2013, **3**, 882–889.
- 16 J. Yu, B. Yang and B. Cheng, *Nanoscale*, 2012, 4, 2670– 2677.
- 17 Y. Zhou, Y. Wang, T. Wen, S. Zhang, B. Chang, Y. Guo, J. *Colloid Interf. Sci.*, 2016, **467**, 97–104.
- 18 T. Li, G. Chen, C. Zhou, Z. Shen, R. Jin and J. Sun, *Dalton Trans.*, 2011, 40, 6751–6758.
- 19 X. Xiao, R. Hao, M. Liang, X. Zuo, J. Nan, L. Li and W. Zhang, J. Hazard Mater., 2012, 233-234, 122–130.
- 20 L. Ye, J. Liu, Z. Jiang, T. Peng and L. Zan, *Appl. Cata. B*, 2013, **142-143**, 1–7.
- 21 X. Wei, H. Cui, S. Guo, L. Zhao and W. Li, *J. Hazard Mater.*, 2013, **263**, 650–658.
- 22 L. Wang and W. A. Daoud, Appl. Surf. Sci., 2015, 324, 532–537.
- 23 H. Liu, Y. Su, Z. Chen, Z. Jin and Y. Wang, J. Hazard Mater., 2014, 266, 75–83.
- 24 W. Liu, J. Cai and Z. Li, ACS Sustain. Chem. Eng., 2015, **3**, 277–282.
- 25 Y. Hsu, S. Lu and Y. Lin, Adv. Funct. Mater., 2005, 15, 1350–1357.
- 26 S. Xie, X. Lu, T. Zhai, J. Gan, W. Li, M. Xu, M. Yu, Y. Zhang, *Langmuir*, 2012, 28, 10558–10564.
- 27 J. Zhang, J. Yu, M. Jaroniec, *Nano lett.*, 2012, **12**, 4584–4589.
- 28 N. Zhang, S. Liu and Y. Xu, *Nanoscale*, 2012, 4, 2227– 2238.
- 29 S. Liu, N. Zhang and Y. Xu, Part. Part. Syst. Charact., 2014, 31, 540–556.
- 30 B. F. Caruso, Adv. Mater., 2001, 13, 11–22.
- 31 H. Mcdaniel, P. E. Heil, C. Tsai, K. K. Kim and M. Shim, ACS Nano, 2011, 5, 7677–7683.
- 32 V. A. Online, Y. Yu, C. Cao, H. Liu, P. Li, F. Wei, Y. Jiang and W. Song, J. Mater. Chem. A, 2014, 2, 1677–1681.
- 33 Y. Huang, H. Li, M. Balogun, W. Liu, Y. Tong, X. Lu and H. Ji, ACS Appl. Mater. Interf., 2014, 6, 22920–22927.
- 34 Y. Zhou, Y. Wang, T. Wen, B. Chang, Y. Guo, Z. Lin and B. Yang, *J. Colloid Interf. Sci.*, 2016, **461**, 185–194.
- 35 X. Wu, G. Siu, C. Fu and H. C. Ong, *Appl. Phys. Lett.*, 2001, **78**, 2285.
- 36 S. Weng, B. Chen, L. Xie, Z. Zheng and P. Liu, *J. Mater. Chem. A*, 2013, **1**, 3068–3075.
- 37 K. Bijanzad, A. Tadjarodi, M. M. Khiavi and O. Akhavan, *Physica B*, 2015, **475**, 14–20.
- 38 Z. Deng, F. Tang and A. J. Muscat, *Nanotechnology*, 2008, 19, 295705.
- 39 Y. Zhu, D. Xu and M. Meng, J. Mater. Sci., 2014, 50, 1594–1604.
- 40 J. Yu, S. Liu and H. Yu, J. Cata., 2007, 249, 59-66.
- 41 Z. Jia, F. Wang, F. Xin and B. Zhang, *Ind. Eng. Chem. Res.*, 2011, **50**, 6688–6694.

- 42 H. Fu, S. Zhang, T. Xu, Y. Zhu, J. Chen, *Environ. Sci. Technol.*, 2008, **42**, 2085–2091.
- 43 Z. He, C. Sun, S. Yang, Y. Ding, H. He, Z. Wang, *J. Hazard Mater.*, 2009, **162**, 1477–1486.
- 44 K. Yu, S. Yang, H. He, C. Sun, C. Gu, Y. Gu, *J. Phys. Chem. A*, 2009, **113**, 10024–10032.
- 45 L. Ye, Y. Su, X. Jin, H. Xie and C. Zhang, *Environ. Sci.*: *Nano*, 2014, **1**, 90–112.
- 46 J. Shang, W. Hao, X. Lv, T. Wang, X. Wang, Y. Du, S. Dou, T. Xie, D. Wang and J. Wang, ACS Cata., 2014, 4, 954–961.
- 47 W. W. Lee, C. Lu, C. Chuang, Y. Chen, J. Fu, *RSC Adv.*, 2015, **5**, 23450–23463.
 - K. Jiao, X. Yu, Z. Liu, P. Kuang, Y. Zhang, *RSC Adv.*, 2015, **5**, 16239–16249.
 - R. G. Pearson, *Inorg. Chem.*, 1988, **27**, 734–740.
 - S. Brook and N. York, *Am. Mineral.*, 2000, **85**, 543–556.
- 51 J. Cao, B. Xu, B. Luo, H. Lin and S. Chen, *Cata. Commun.*, 2011, **13**, 63–68.
- 52 L. Kong, Z. Jiang, T. Xiao, L. Lu, M. O. Jones and P. P. Edwards, *Chem. Commun.*, 2011, **47**, 5512–5514.

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Graphical Abstract



A family of heterostructured core-shell $Cd_{0.2}Zn_{0.8}S@BiOX$ (X = Cl, Br, I) microspheres with adjustable bandgaps, enhanced stability and visible-light-driven photocatalytic performance were fabricated via a facile solvothermal route.