Synergetic Ag$_2$S and ZnS quantum dots as the sensitizer and recognition probe: A visible light-driven photoelectrochemical sensor for the “signal-on” analysis of mercury (II)

Lixiang Zhang$^{a,b}$, Pan Li$^b$, Luping Feng$^{b,c}$, Xi Chen$^{b,c}$, Jiattian Jiang$^b$, Sheng Zhang$^b$, Chunxian Zhang$^b$, Anchoa Zhang$^d$, Guofu Chen$^a$, Hua Wang$^{a,b,c,1,*}$

$^a$ School of Environment, Harbin Institute of Technology, Harbin, Heilongjiang 150090, PR China
$^b$ Institute of Medicine and Materials Applied Technologies, College of Chemistry and Chemical Engineering, Qufu Normal University, Qufu, Shandong 273165, PR China
$^c$ School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, Heilongjiang 150090, PR China
$^d$ School of Mechanical and Power Engineering, Henan Polytechnic University, Jiaozuo, Henan 454000, PR China

GRAPHICAL ABSTRACT

ABSTRACT

A visible-light-driven photoelectrochemical (PEC) sensor has been developed for the “signal-on” analysis of Hg$^{2+}$ by the synergetic combination of low-bandgap Ag$_2$S and wide-bandgap ZnS quantum dots (QDs). Ag$_2$S QDs were synthesized with bead-chain-like structure by the self-assembly route and further covalently bound with ZnS QDs to be coated onto the indium tin oxide (ITO) electrodes. It was discovered that the ZnS@Ag$_2$S-modified electrodes could display the visible-light-driven PEC behavior, of which Ag$_2$S and ZnS QDs could act as the PEC sensitizer and Hg$^{2+}$-recognition probe, respectively. More importantly, the photocurrent responses of the developed electrodes could be specifically turned on in the presence of Hg$^{2+}$ under the visible-light irradiation, presumably due to that Hg$^{2+}$ might conduct a Zn-to-Hg exchange on ZnS QDs to trigger the formation of HgS/ZnS@Ag$_2$S heterojunction towards the enhanced electron-hole separation. The as-prepared PEC sensor could facilitate the detection of Hg$^{2+}$ with concentrations ranging from 0.010–1000 nM, with a detection limit of about 1.0 pM. Besides, the feasibility of practical applications of the developed PEC analysis strategy was ver-

https://doi.org/10.1016/j.jhazmat.2019.121715

Received 27 September 2019; Received in revised form 5 November 2019; Accepted 17 November 2019

Available online 19 November 2019

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1. Introduction

Heavy metal ions, especially mercury ions, may be accumulated with excessive amounts in human body causing some serious diseases such as pneumonia, enteritis, and bronchitis (Zhou et al., 2010; Babaei et al., 2019; Elsebai et al., 2017). At present, many analysis methods have been applied for the determination of Hg$^{2+}$ including atomic absorption spectrometry (Butler et al., 2006), inductively coupled plasma-mass spectrometry (Li et al., 2006), surface-enhanced Raman scattering (Chen et al., 2014), fluorometry (Wang et al., 2015a), and colorimetry (Yan et al., 2015). These classic Hg$^{2+}$ analysis methods may be mostly suffered from some drawbacks of either of complicated operation and bulky devices, or low detection sensitivity and poor selectivity. Therefore, developing a simple, sensitive, selective, and especially field-deployable detection method for evaluating trace Hg$^{2+}$ has become an attractive but challenging target to pursue.

Photoelectrochemical (PEC) detection strategies are newly emerged electroanalysis technologies using photoactive species that are excited to produce photocurrents of detection signals. They can feature some advantages over the conventional electrochemical detection methods such as low cost, uncomplicated device, and simple sample preparation. Especially, the signal output format of the PEC analysis methods can separate the excitation source (light) and the detection signal (photocurrent) so as to ensure the higher analysis sensitivity and selectivity. During the past decades, various PEC analysis platforms have been applied in many research fields including immunoassays, DNA analysis, enzymatic biosensing, chemical oxygen demand, glucose, small organic molecules, antibiotics and heavy metals detections (Zhao et al., 2015, 2014a; Zhao et al., 2014b, 2017; Peng et al., 2016a; Peng et al., 2019, 2017; Pang et al., 2015; Peng et al., 2018a; Peng et al., 2019b). In particular, the PEC detection methods have also been employed using some functional probes to probe Hg$^{2+}$ ions (Zhang et al., 2016; Wen et al., 2015; Han et al., 2015; Li et al., 2014). For example, Zhang et al. developed a PEC detection method for sensing Hg$^{2+}$ using Au-Ag nanorods-modified TiO$_2$ nanosheets (Zhang et al., 2016). Wen and colleagues reported a PEC analysis strategy for sensing Hg$^{2+}$ using CdTe quantum dots (QDs) (Wen et al., 2015). Chen’s group has proposed an energy transfer-based PEC method for probing Hg$^{2+}$ with CdS QDs and Au nanoparticles (Han et al., 2015). These PEC detection methods, however, are generally proposed by the unfavourable photocurrent-“turn off” way, which may be challenged by the serious background inferences leading to the low detection selectivity and sensitivity (Wang et al., 2015b). Alternatively, some efforts have tried to design the PEC detection methods for sensing Hg$^{2+}$ with “turn-on” signals of great interest (Wang et al., 2014, 2018). For example, a “signal-on” PEC sensor has been fabricated for the sensitive Hg$^{2+}$ detections using ZnS QDs (Wang et al., 2014, 2018). Unfortunately, a challenge may be currently encountered regarding the use of n-type semiconductor probes of wide band gaps with photocurrent responses triggered only under ultraviolet irradiation. It is well established that the introduction of narrow band-gap semiconductors like Ag$_2$S QDs as cocatalysts may effectively enhance the visible light absorption and separation of electron-hole pairs of wide band-gap semiconductors (i.e., ZnS QDs) to achieve the improved photocatalysis (Yang et al., 2014; Reddy et al., 2015). For example, Ag$_2$S QDs, with a low bandgap can be responsive to near-infrared (NIR) light, which has been commonly utilized in the biological imaging and sensing fields (Hong et al., 2012; Li et al., 2018). Nevertheless, it has hardly been employed for the construction of the PEC analysis platforms for detecting heavy metal ions like Hg$^{2+}$ to date.

Inspired by these pioneering works above, in the present work, low-bandgap Ag$_2$S QDs were synthesized for the first time with bead chain-like structure by the self-assembly route and further coated onto the indium tin oxide (ITO) electrodes, followed by covalently coupling with wide-bandgap ZnS QDs. As expected, the yielded ZnS@Ag$_2$S-modified electrodes were found to present powerful visible-light PEC performance, in which Ag$_2$S QDs and ZnS QDs could act as the PEC sensitizers and Hg$^{2+}$ probes, respectively. More importantly, the photocurrent responses of the developed PEC sensor could be specifically turned on in the presence of Hg$^{2+}$ under the visible-light irradiation, presumably due to that the introduction of Hg$^{2+}$ might conduct a Zn-to-Hg exchange on ZnS QDs so as to trigger the formation of HgS/ZnS@Ag$_2$S heterojunction for enhanced charge separation. A visible light-driven PEC detection method has thereby been developed for probing Hg$^{2+}$ in the environmental samples with high analysis sensitivity and selectivity. To the best of our knowledge, this is the first report on the design of visible-light-driven PEC analysis platform for the “signal-on” evaluation of Hg$^{2+}$ in environmental water by the synergetic combination of Ag$_2$S and ZnS QDs separately as the PEC sensitizer and recognition probe. Importantly, the so proposed fabrication strategy synergistically using two kinds of functional materials of low-bandgap Ag$_2$S and wide-bandgap ZnS QDs may provide a general model for the design of various PEC sensors for sensing different kinds of analytes like heavy metal ions.

2. Experimental section

2.1. Reagents and materials

Silver nitrate, zinc nitrate, absolute ethanol, ethylene glycol, aceticone, and triethanolamine (TEA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Phosphate buffer saline (PBS) solution and thiaoacetamide (TAA) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Nafion solution (5.0 %), cysteamine, 3-Mercaptopropionic acid (3-MPA), ethylenediaminetetraacetic acid (EDTA), 1-ethyl-3-[3-(dimethylamino)-propyl] carbodiimide (EDC) and N-hydroxy succinimide (NHS) were purchased from Sigma-Aldrich (Beijing, China). All other reagents were of analytical grade and employed without further treatment. Deionized water (> 18 Mohm) was obtained from an ultrapure water system (Pall, USA).

2.2. Characterization of functional materials

High resolution transmission electron microscope (HRTEM, JEOL/JEM-20100PLUS, Japan), field-emission scanning electron microscope (SEM, JEOL/JSM-6700 F and Carl Zeiss AG/Sigma 500 V P, Germany), equipped with the energy dispersive spectrometer (EDS, EDX Genesis), X-ray diffractometer (XRD, PANalytical/X’pert3, Netherlands), Fourier transform infrared (FTIR) spectrometer (Bruker Tensor 27, Germany), X-ray photoelectron spectroscopy (XPS, Thermo Fisher/Escalab 250Xi, USA), UV–vis diffuse reflectance spectracta (DRS, Shimadzu/UV-3600, Japan), FluoroMax-4 fluorescence spectrometer (Horiba, France), and inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent-725, USA) were utilized to characterize the as-prepared materials. Moreover, the characterization with electrochemical impedance spectroscopy (EIS) was carried out on an electrochemical workstation (CHI 760D, China) with the frequency range of 0.010 Hz and 100 kHz and an AC voltage magnitude of 5.0 mV in 0.1 M KCl electrolyte. Further, Mott-Schottky (M-S) plots with amplitude of 10 mV and different frequency values were obtained by the electrochemical measurements to evaluate the flat band potential of the
semiconductors. Besides, the generalized-gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) correction was applied to calculate the work function using CASTEP software according to the density functional theory (DFT).

2.3. Synthesis of Ag₂S and ZnS QDs

The synthetic procedures of Ag₂S and ZnS QDs are depicted in Scheme 1A. The carboxyl-derivatized Ag₂S QDs with bead chain-like structure were synthesized by a modified self-assembly route reported previously (Li et al., 2018). Briefly, silver nitrate (0.30 mmol) and 3-MPA (7.0 mmol) were mixed with ethylene glycol (4.5 mL) under stirring vigorously. The reaction vessel was degassed before refilling with high purity nitrogen. Furthermore, the mixture was cultivated at 145 °C for 30 min and then naturally cooled down to room temperature, followed by purification by high-speed centrifuging. Finally, the products were harvested by freeze dryer yielding the powder of carboxyl-derivatized Ag₂S QDs that were stored in dark.

The amine-derivatized ZnS QDs were synthesized by a hydrothermal route. Typically, an aliquot of 0.38 mmol of zinc nitrate was added into 70 mL ethanol containing 0.38 mmol of TAA to be stirred for 30 min. Then, the mixture was transferred into a Teflon-lined autoclave (100 mL in capacity) and then heated to 180 °C for 3.0 h. After cooling down to room temperature, the precipitates were purified by the high-speed centrifuging and further washed with ethanol-water mixture for three times. After being dried at 60 °C overnight, white amine-derivatized ZnS powders were yielded to be stored in dark.

2.4. Fabrication of ZnS@Ag₂S-modified electrodes

The step-by-step fabrication procedure of ZnS@Ag₂S-modified electrode was disclosed in Scheme 1B, in which carboxyl-derivatized Ag₂S QDs were modified onto the ITO electrodes followed by the covalent immobilization of amine-derivatized ZnS QDs by the classical procedure of EDC/NHS crosslinking chemistry. Typically, ITO slices (1.0 × 1.0 cm²) were sonicated separately in acetone, 1.0 M NaOH, ethanol, and water, each for 15 min. Then, an aliquot of 20 μL of carboxyl-derivatized Ag₂S solutions (5.0 mg mL⁻¹) was separately drop-cast onto ITO slices. After being dried at 30 °C in a vacuum drying oven, the resulting Ag₂S QDs-modified ITO electrode was immersed in a mixed solution of EDC (10 mg mL⁻¹) and NHS (5.0 mg mL⁻¹) for 60 min to activate the carboxyl groups on Ag₂S QDs. Then, 5.0 mg amine-derivatized ZnS powder was dispersed ultrasonically in 1.0 mL water. Furthermore, an aliquot of 20 μL of the resulting dispersion (5.0 mg mL⁻¹) above was dropped onto the surface of the activated electrodes for 30 min at room temperature. After that, the electrodes were rinsed with water, and then dried at 30 °C under vacuum state. Besides, the ZnS-to-Ag₂S molar ratios on the modified electrodes were determined by using ICP-OES.

Scheme 1. Schematic illustration of (A) the synthetic process of carboxyl-derivatized Ag₂S and amine-derivatized ZnS QDs using 3-MPA and TAA, respectively; (B) the immobilization procedure of Ag₂S and ZnS QDs onto the ITO electrodes (ZnS@Ag₂S-modified electrodes) for the photoelectroanalysis of Hg²⁺; and (C) the mechanism of photocurrent responses of ZnS@Ag₂S-modified electrodes, showing the band structures of HgS/ZnS@Ag₂S heterojunction and charge separation under the visible-light illumination.
2.5. PEC detections of Hg$^{2+}$

The PEC measurements were performed with a home-made PEC analysis system, in which a 500 W Xe lamp equipped with 420 nm cutoff filter ($\lambda \geq 420$ nm) was used as the irradiation source. The photocurrent responses were measured on a CHI 760D electrochemical workstation at room temperature using a conventional three-electrode system, of which the ZnS@Ag$_2$S-modified ITO electrode, the Ag/AgCl electrode, and the platinum wire were utilized as the working electrode, the reference electrode, and the auxiliary electrode, respectively. All of the photocurrent measurements were carried out at a constant potential of 0.80 V vs reversible hydrogen electrode (RHE). Herein, the Hg$^{2+}$ of different concentrations were detected by the ZnS@Ag$_2$S-modified electrodes in PBS solution (pH 7.4) containing 0.10 M TEA, of which the photocurrent responses were recorded. Of note, prior to the measurement experiments, the PBS solutions should be deaerated with nitrogen for several minutes, and then a N$_2$ atmosphere should be kept during the entire experimental process.

3. Results and discussion

3.1. Characterization of ZnS@Ag$_2$S nanocomposites

The morphological structures of the prepared Ag$_2$S QDs, ZnS QDs, and ZnS@Ag$_2$S nanocomposites were comparably investigated by scanning electron microscope (SEM) imaging. Fig. 1A manifests the SEM image of Ag$_2$S QDs, showing the bead chains-like morphological structure with numerous nanodots, which morphological structures could be well maintained in ZnS@Ag$_2$S nanocomposites modified on the ITO electrodes as revealed in Fig. S1A. Moreover, an energy dispersive spectrometer (EDS) mapping analysis was performed for bead chains-like Ag$_2$S QDs, confirming the identified inclusion of Ag and S elements (Fig. 1B). It should be pointed out that the Ag and S elements might be unevenly distributed to some degree, presumably due to the ultrasonic dispersion treatment that might have broken part of Ag$_2$S QDs in addition to the light-sensitive merit of Ag$_2$S QDs that might be partly decomposed under the EDS mapping. Yet, the EDS mapping images suggest that the elements of Ag, Zn, and S could be uniformly distributed in the ZnS@Ag$_2$S nanocomposites on the ITO electrodes because of ZnS QDs coating (Fig. S1B). Furthermore, high resolution transmission electron microscope (HRTEM) imaging (Fig. 2) with the corresponding grain diameter distribution profile (Fig. S2) was comparably performed for Ag$_2$S QDs, ZnS QDs, and ZnS@Ag$_2$S nanocomposites. Fig. 2A illustrates the HRTEM image of Ag$_2$S QDs, indicating that the nanodots with an average size of about 9.0 nm in diameter (Fig. S2A) could be self-assembled towards the bead chains. Also, as can be seen from the Fig. 2B, the interplanar distance of 0.20 and 0.24 nm of the materials can be clearly observed agreeing well with the lattice fringe of the (211) and (200) crystal plane of Ag$_2$S QDs, respectively (Yang et al., 2014; Reddy et al., 2015). Moreover, one can note both from Fig. 2C and Fig. S2B that ZnS QDs could present the spherical structure with an average size of about 5.5 nm in diameter. The lattice fringes of ZnS QDs could be clearly observed with the lattice fringes spacing of 0.19 and 0.31 nm corresponding to the (220) and
(111) crystal plane of ZnS QDs (Fig. 2D), respectively (Yang et al., 2014; Reddy et al., 2015). Furthermore, the HRTEM image of ZnS@Ag2S nanocomposites reveals that many spots of agglomerated ZnS QDs were uniformly distributed on the surface of Ag2S QDs, verifying the production of ZnS@Ag2S nanocomposites (Fig. 2E). Of note, the magnified HRTEM image discloses that two different interplanar spacings were observed, which should belong to the (211) plane of Ag2S and (111) plane of ZnS QDs, respectively (Fig. 2F). Besides, the EDS analysis of ZnS@Ag2S nanocomposites was performed, the elements of silver, zinc, and sulfur were clearly identified, which may further confirm the coexistence of Ag2S and ZnS QDs in ZnS@Ag2S nanocomposites (Fig. S3).

The ZnS@Ag2S nanocomposites were further explored by the FTIR spectra (Fig. 3A). The characteristic peaks of carboxylate groups at ∼1715 cm\(^{-1}\) (C=O stretch) and ∼1255 cm\(^{-1}\) (C–O stretch) of Ag2S QDs were observed in the FTIR spectrum (curve a). Similarly, a peak at ∼1640 cm\(^{-1}\) was witnessed (curve c), which may be attributed to the amide II band (the coupling of stretching vibrations of C–N and bending vibrations of N–H) (Li et al., 2018), thus proving the formation of ZnS@Ag2S nanocomposites.
The crystalline structures of ZnS QDs, Ag₂S QDs, and ZnS@Ag₂S nanocomposites were analyzed by the X-ray diffractometer (XRD), with the results shown in Fig. 3B. Accordingly, Ag₂S QDs could show the weak and undistinguishable diffraction peaks owing to its small size and amorphous surface ligands, in consistence with the mononclic Ag₂S QDs reported elsewhere (Jiang et al., 2015). Moreover, the obvious diffraction peaks separately at the 2θ values of 28.61°, 33.15°, 47.59°, and 56.47° could be observed for ZnS QDs, which can match well with the standard pattern of cubic ZnS (JCPDS: 65-0309), confirmed the coating of ZnS QDs on the ZnS@Ag₂S nanocomposites.

To explore the surface composition and chemical states of the as-prepared ZnS@Ag₂S nanocomposites, X-ray photoelectron spectroscopy (XPS) analysis was carried out, with the results shown in Fig. 4. The full scan spectrum in Fig. 4A shows the presence of the C, O, N, Ag, Zn, and S peaks, where the peaks of C, O, and N should come from the carboxyl and amino groups onto the samples. Moreover, Fig. 4B shows that the binding energies of Ag 3d₃/₂ and Ag 3d₅/₂ in 373.9 eV and 367.1 eV are the characteristic signals of Ag⁺ in Ag₂S products (Di et al., 2019). Also, one can note from Fig. 4C that two individual peaks located at 1044.8 and 1021.6 eV can be assigned to Zn 2p₁/₂ and Zn 2p₃/₂, revealing that the chemical state of Zn is the bivalent one. Additionally, Fig. 4D depicts the peak at 161.4 eV belongs to S²⁻ 2p₃/₂ in a zinc-sulfur bond and silver-sulfur bond in the nanocomposites (Zhang et al., 2013). Consequently, the XPS analysis data further indicate the nanocomposites can consist of Ag₂S and ZnS QDs. It should be pointed out that the obtained binding energy of Ag 3d₅/₂ positively shifted while the binding energy of Zn 2p₃/₂ negatively shifted in comparison with NIST X-ray Photoelectron Spectroscopy Database, which may indicate that the electrons might migrate from the ZnS QDs to Ag₂S QDs because of their different Fermi levels (Fu et al., 2018).

The UV–vis diffuse reflectance spectra (DRS) of ZnS@Ag₂S nanocomposites were measured in comparison with those of ZnS and Ag₂S QDs (Fig. 5A). It was observed that Ag₂S QDs with the narrow band gap could display a strong absorption capacity in the wavelength range of 200–1000 nm, whereas ZnS QDs with the wide band gap exhibited the absorption edges of around 350 nm. As expected, the combination of Ag₂S and ZnS QDs could obtain an enhanced absorbance capacity, showing an absorption edge of around 1100 nm, indicating that Ag₂S QDs could act as a visible-light photosensitizer for ZnS QDs. The band gap values of the semiconductors and composites were thereby calculated by the equation: $\alpha \nu = A(\nu - E_g)^n/2$, where $\alpha$ is the absorption coefficient, $h$ is Planck constant, $\nu$ is light frequency, $A$ is a proportionality constant, $E_g$ is the band gap, and $n$ is decided by the transition type of the semiconductor, with the data shown in Fig. 5B. Accordingly, the $E_g$ of Ag₂S and ZnS QDs were estimated to be 1.15 and 3.57 eV, respectively.

Moreover, the electrochemical measurements were carried out for Ag₂S and ZnS QDs to determine their flat band potentials by the Mott-Schottky (M-S) plotting (Fig. 5C). According to the M-S equation, the flat band potentials of Ag₂S and ZnS QDs were obtained to be 0.050 and -0.96 eV, respectively, which are in good agreement with those of previous reports (Weng et al., 2014). Considering that the conduction band potentials ($E_{cb}$) of n-type semiconductors are generally approximate to the flat band potentials, the $E_{cb}$ of Ag₂S and ZnS were thus estimated to be 0.050 and -0.96 eV, respectively. According to the equation $E_{vb} = E_{cb} + E_g$, the valence band potential ($E_{vb}$) values were calculated to be 1.2 and 2.61 eV, respectively.

3.2. PEC behavior of ZnS@Ag₂S-modified electrodes

Fig. 6A shows a comparison of photocurrent responses among the electrodes modified separately with Ag₂S QDs, ZnS QDs, and ZnS@Ag₂S composites. It was found that the Ag₂S-modified electrode could generate a photocurrent density of 0.74 μA·cm⁻², whereas the ZnS-modified one could produce a negligibly low photocurrent density because of the wide band gap of ZnS QDs (3.57 eV). Importantly, a much higher photocurrent density of 1.04 μA·cm⁻² could be obtained for the ZnS@Ag₂S-modified electrode, indicating that Ag₂S QDs could act as the PEC sensitizer for ZnS QDs to conduct the synergetic effect. Furthermore, the photocurrent densities of ZnS@Ag₂S-modified electrode
were recorded under the visible light irradiation repeated at the time interval of 10 s (Fig. 6B). To our surprise, the photocurrent densities showed only a 4.23 % decrease after 40 on-off cycles, indicating that the ZnS@Ag2S-modified electrodes could display the considerably stable photocurrent responses to promise for the construction of the robust PEC sensors afterwards.

Moreover, the separation and recombination tendency of the photogenerated electron-hole pairs of ZnS@Ag2S nanocomposites were comparably explored by the analysis of the photoluminescence (PL) spectra (Fig. 6C). It was observed that the ZnS@Ag2S nanocomposites could present two emission peaks at 586 nm and 866 nm, which could correspond to the emissions of photo-carriers generated by ZnS and Ag2S QDs, respectively. By comparison, the ZnS@Ag2S nanocomposites could exhibit the much lower peak intensity than ZnS and Ag2S QDs.

![Fig. 5.](image1)

**Fig. 5.** (A) UV–vis DRS spectra of Ag2S QDs, ZnS QDs and ZnS@Ag2S nanocomposites. (B) The plots of \((\alpha h \nu)^2\) versus \(h \nu\) for Ag2S and ZnS; the Mott–Schottky plots for (C) Ag2S QDs and (D) ZnS QDs.

The stability tests of photocurrent responses of ZnS@Ag2S nanocomposites when light irradiation was turned on and off at an interval time of 10 s (Fig. 6B). (C) PL spectra of Ag2S QDs, ZnS QDs and ZnS@Ag2S nanocomposites (excitation at 488 nm) and (D) the electrochemical impedance spectra of different samples indicated.

![Fig. 6.](image2)

**Fig. 6.** (A) Photocurrent responses of different samples indicated in PBS containing TEA (0.10 M) under the visible-light irradiation. (B) The stability tests of photocurrent responses of ZnS@Ag2S nanocomposites when light irradiation was turned on and off at an interval time of 10 s. (C) PL spectra of Ag2S QDs, ZnS QDs and ZnS@Ag2S nanocomposites (excitation at 488 nm) and (D) the electrochemical impedance spectra of different samples indicated.
alone, indicating a lower recombination rate of photogenerated electron-hole pairs could be expected for the ZnS@Ag 2S nanocomposites (Fu et al., 2018).

Besides, electrochemical impedance spectroscopy (EIS) was utilized to investigate the change of charge transfer resistance of ZnS@Ag 2S nanocomposites by taking ZnS and Ag2S QDs for comparison (Fig. 6D). Herein, the semicircle diameters may reflect the charge transfer resistance between the semiconductor and electrolyte interface, by which a smaller radium in the EIS Nyquist plot can mean a faster mobility of photogenerated electrons and a more efficient electrons-holes (e− - h+)

separation (Lim et al., 2014). Accordingly, the arc radium on the Nyquist plots of the ZnS@Ag2S-modified electrode is much smaller than those of the Ag2S and ZnS-modified electrodes. The results imply that the introduction of ZnS QDs onto the surface of Ag2S QDs could achieve the enhanced separation efficiency and interfacial charge transfer of photo-induced carriers.

3.3. PEC sensing mechanism

The work functions of Ag2S QDs, ZnS QDs, and HgS were calculated to tentatively explore their charge migration behaviors (Fig. 7). According to the XRD and HRTEM analysis and the Joint Committee on Powder Diffraction Standards cards (JCPDS cards), the (211) crystal face of Ag2S (JCPDS:65-4429), (111) crystal face of ZnS (JCPDS:65-0309), and (200) crystal face of HgS (JCPDS:65-4299) were chosen as the crystal models to calculate the work functions. Accordingly, the work functions of Ag2S (211), ZnS (111) and HgS (200) are obtained to be 4.86, 5.47, and 6.22 eV, respectively. These results reveal that the Ag2S (211) surface can show the lowest Fermi energy (E_F), whereas HgS (200) surface has the highest one. Consequently, once ZnS QDs were anchored onto Ag2S QDs, the electrons would transfer from Ag2S QDs to ZnS QDs until the Fermi energies reach the same level. Moreover, when the ZnS@Ag2S-modified electrodes were applied for the PEC detection of Hg2+ in solutions, HgS could be in situ formed on the surface of ZnS QDs through the Zn-to-Hg cation exchange, as reported elsewhere (Qu et al., 2014; Liu et al., 2019), which has been further confirmed by the XPS analysis (Fig. 54). Due to the HgS can display the higher E_F than ZnS QDs and Ag2S QDs, the electrons would transfer from Ag2S QDs to ZnS QDs and then HgS QDs until the Fermi energies reach the same level. Owing to the quantum size effect and the well-known shortcoming of DFT in describing the excited states (Jiang et al., 2015; Lin et al., 2015; Zhou et al., 2019), this result is not well consistent with the charge transfer as revealed by the XPS results aforementioned (Fig. 4).

To explore further the sensing mechanism for the enhanced

![Fig. 7. DFT analysis results of optimized crystal structure, Fermi levels, and work functions of Ag2S (211), ZnS (111) and HgS (200) calculated.](image-url)
photocurrent responses of the ZnS@Ag2S-modified electrodes to Hg2⁺, the energy bands of AgS QDs and ZnS QDs were investigated. The schematic diagram of main sensing principle is illustrated in Scheme 1C. According to the results of M-S equation mentioned above, herein, the band edges of AgS QDs (E_Cb = 0.050 eV, E_VB = 1.2 eV) and ZnS QDs (E_Cb = -0.96 eV, E_VB = 2.61 eV) could be excited to generate the photoinduced carriers under visible light illumination. Whereas, most of the generated holes and electrons might recombine rapidly, leading to a relatively low PEC performance for ZnS QDs. Moreover, the conduction band (CB) of ZnS QDs with wide band gap is higher than that of AgS QDs with narrow bang gap. As a result, once ZnS QDs are coupled with AgS QDs, the excited electrons on the CB of ZnS QDs would be injected into the more positive CB of AgS QDs until the Fermi energies reach the same level, which should be then transferred to the ITO electrodes. Meanwhile, the h⁺ on the valence band (VB) of ZnS QDs should shift to that of AgS QDs, which should be scavenged by triethanolamine (TEA, electron donor). A much higher photocurrent can be observed for the ZnS@Ag2S-modified electrode. Therefore, when the ZnS@Ag2S-modified electrode was utilized as the PEC sensor for sensing Hg²⁺, the enhanced photocurrent could be achieved by the in-situ formation of HgS on the surface of ZnS QDs through the selective Zn-to-Ag₂S exchange, due to the solubility constant (K_sp) of HgS (4.0 × 10⁻⁵³ – 2 × 10⁻²⁵) is much lower than that of ZnS (2 × 10⁻²²) (Wang et al., 2018). Of note, the in-situ formed HgS is a p-type semiconductor with a narrow bandgap of 2.01 eV, showing the CB and VB edge of 0.0 and 2.01 eV, respectively (Wang et al., 2018). According to the calculated energy band of HgS, hence, the electrons should transfer from HgS to ZnS QDs and then AgS QDs, whereas the h⁺ from ZnS QDs should transfer to AgS QDs and HgS, which can be scavenged by TEA (electron donor). As a result, a HgS/ZnS@Ag₂S heterojunction (build-in electric field) would be formed at the interface between negatively charged ZnS QDs and positively charged HgS due to the matched band structures, thus achieving the enhanced separation of electrons and holes and reducing the recombination rate among HgS, ZnS QDs and AgS QDs. A visible-light-driven PEC sensor can thereby be proposed by the synergetic combination of AgS and ZnS QDs for the “signal-on” analysis of Hg²⁺, in which AgS and ZnS QDs should act as the PEC sensitizers and Hg²⁺-recognition probe, respectively.

3.4. Applications for PEC Hg²⁺ analysis

It is generally recognized that metal sulfide (MS) may often encounter with the photochemical corrosion under light illumination by the reaction equation: 2h⁺ + MS → M²⁺ + S (Wang et al., 2018). To avoid such a photocorrosion challenge and especially obtain the stable photocurrent of metal sulfide, an electron donor should be necessarily introduced to act as the scavenger for the holes on the surface of metal sulfide to inhibit the photocorrosion. TEA was thus chosen as the electron donor to explore the TEA-dependent photocurrent responses of the ZnS@Ag₂S-modified electrodes (Fig. S5A). It was found that the photocurrent densities of the ZnS@Ag₂S-modified electrodes could increase as increasing TEA concentrations until 0.10 M, which was chosen as the optimal TEA concentration in the PEC experiments. Moreover, the relative photocurrent increments of the ZnS@Ag₂S-modified electrodes to Hg²⁺ ions were explored in TEA-containing PBS under different detection conditions including the ZnS-to-Ag₂S molar ratios, ZnS@Ag₂S dosages, potentials, and pH values (Fig. S5B-E). Herein, the relative photocurrent increment is defined as (I-I₀)/I₀, where I and I₀ represent the photocurrents of the ZnS@Ag₂S-modified electrodes in the presence and absence of Hg²⁺, respectively. Fig. S5B shows that the relative photocurrent increments can increase with increasing ZnS-to-Ag₂S molar ratios till 1/1.01, over which the relative photocurrent increments would gradually decrease, showing the optimal one of 1/1.01 to be selected in the experiments for Hg²⁺ detections. Similarly, the ZnS@Ag₂S-modified electrodes could present the highest relative photocurrent increments in sensing Hg²⁺ at the ZnS@Ag₂S dosage of 5.0 mg mL⁻¹ (Fig. S5C) and potential of 0.80 V vs RHE (Fig. S5D). In addition, the influences of pH values on the PEC responses were explored with the results depicted in Fig. S5E, showing the optimal pH of 7.4. Herein, Zn₅ (Hg²⁺-recognition probe) may be unstable at lower pH values (Qu et al., 2014), whereas Hg²⁺ may form HgO precipitate at higher pH values. As a result, the modified electrodes should obtain the largest photocurrent responses to Hg²⁺ at the neutral conditions of pH 7.4.

Under the optimized detection conditions, the developed ZnS@Ag₂S-modified electrodes were applied for sensing Hg²⁺ with different concentrations in buffer (Fig. 8). It was found that the photocurrent densities of ZnS@Ag₂S-modified electrodes could increase with the increasing Hg²⁺ concentrations (Fig. 8A). A linear relationship between the relative photocurrent increments of (I-I₀)/I₀ versus the logarithm of Hg²⁺ concentrations was thus achieved ranging from 0.0050 to 1000 nM (Fig. 8B), with the limit of detection (LOD) of about 1.0 pM, estimated by 3σ rule. Moreover, a standard deviation was obtained to be 2.4 % for the six replicate Hg²⁺ measurements, suggesting a good PEC analysis reproducibility. Also, the storage stability of the ZnS@Ag₂S-modified electrodes were investigated, of which the electrodes were stored in dark for different time intervals to be applied for the photoelectroanalysis of Hg²⁺ (Fig. S6). As expected, no obvious change in the photocurrent responses to Hg²⁺ was observed for the ZnS@Ag₂S-modified electrodes stored even over 12 months, showing a long-term environmental stability. Moreover, the sensing performances of the developed PEC analysis method were compared with these of other kinds of PEC analysis methods for Hg²⁺ reported previously (Zhang et al., 2016; Wen et al., 2015; Han et al., 2015; Wang et al., 2014, 2018; Zhang and Guo, 2012). The analysis results are comparably summarized in Table S1. Accordingly, the developed PEC analysis method with ZnS@Ag₂S nanocomposites presents the better detection performances in terms of detection ranges and LODs.

![Fig. 8](image-url)
The analysis selectivity of the developed PEC sensor was explored by probing different metal ions (Hg$^{2+}$, K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Fe$^{3+}$, Ni$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, and Cu$^{2+}$) with the data shown in Fig. 9A. By comparing with Hg$^{2+}$, the tested cations alone could present negligibly low responses. In addition to the better matched band structures between HgS and ZnS QDs, the high analysis selectivity of the developed PEC sensor in sensing Hg$^{2+}$ may be attributed to that HgS with the lower solubility constant than the common metal sulfides like ZnS (Wang et al., 2018) might be formed on the surface of ZnS QDs through the selective Zn-to-Hg exchange leading to the enhanced photocurrents as aforementioned. Furthermore, one can note from Fig. 9B that when these tested cations were separately coexisted with Hg$^{2+}$, no significant effect was observed on the detection of Hg$^{2+}$ except for Cu$^{2+}$. Fortunately, this Cu$^{2+}$ interference could be circumvented by adding a strong chelating agent of ethylenediaminetetraacetic acid (EDTA), showing a negligibly low response as revealed in Fig. 9B. These above results demonstrate that the developed PEC sensor can present a satisfactory selectivity for the Hg$^{2+}$ detections. To validate the feasibility of practical applications, the developed PEC analysis strategy was further employed to evaluate Hg$^{2+}$ with different levels spiked separately in tap water and lake water. Herein, a comparison of Hg$^{2+}$ analysis results was conducted between the developed PEC sensor and ICP-MS method (Table S2). One can note that the analysis capacity of the developed PEC sensor can be comparable to the classic ICP-MS method, exhibiting the basically consistent results of mean concentrations and recoveries for Hg$^{2+}$ both in tap water and lake water samples. Therefore, the proposed visible-light-driven PEC analysis platform using Ag$_2$S and ZnS QDs separately as the sensitizer and recognition probe can promise for the sensitive evaluation of Hg$^{2+}$ in the environmental samples.

4. Conclusion

In summary, bead chain-like Ag$_2$S QDs were successfully synthesized by the self-assembly route and further covalently coated with ZnS QDs onto the ITO electrodes, resulting in a visible-light-driven PEC analysis platform for the “signal-on” detection of Hg$^{2+}$ in environmental samples. It was discovered that ZnS QDs, which otherwise are hard to be excited to generate photocurrents under visible light, could display the improved photocurrent responses once coupled with Ag$_2$S QDs, which could act as the PEC sensitizer to endow ZnS QDs with the enhanced light absorption and separation of photogenerated electrons and holes. More importantly, the photocurrent responses of the developed ZnS@Ag$_2$S-modified electrodes could be specifically turned on in the presence of Hg$^{2+}$ under the visible-light illumination, presumably due to the selective Zn-to-Hg exchange on ZnS QDs that could act as the recognition probe of Hg$^{2+}$. Importantly, the formation of HgS/ZnS@Ag$_2$S heterojunction could be triggered to expect the enhanced charge separation towards the improved PEC performance of ZnS@Ag$_2$S nanocomposites. A visible light-driven PEC sensor has thereby been constructed for the “signal-on” determination of trace Hg$^{2+}$, with the levels down to 1.0 pM. The developed PEC analysis strategy with synergetic Ag$_2$S and ZnS QDs may promise the potential applications for the evaluation of Hg$^{2+}$ in the fields of environmental monitoring, clinical disease diagnosis, and food safety. Besides, the proposed design route synergistically using two kinds of low-bandgap and wide-bandgap QDs as the PEC sensitizer and Hg$^{2+}$-recognition probe may provide a general model for the fabrications of a variety of visible-light-driven PEC analysis platform for sensing different analytes like heavy metal ions.

Declaration of Interest Statement

The authors declare no competing financial interest.

Acknowledgments

We are grateful to Dr. Anchao Zhang from Henan Polytechnic University for his guidance in theoretical calculation analysis. This study was supported by the National Natural Science Foundation of China (No. 21675099), Major Basic Research Program of Natural Science Foundation of Shandong Province, P. R. China (ZR2018ZC0129), and Science and Technology Development Project of Weihai City (2015DXGJZD002), Shandong Province, P. R. China.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2019.121715.

References


Yang, W., Wang, Y., Zhuang, H., Zhang, J., 2015. DNA-engineered chiroplasmic