Au/ZnS/ZnO Photoelectrochemical Sensor for Sensitive and Selective Cd²⁺ Detection

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Sensitive and selective detection of cadmium ions is important to pollution monitoring and human health. In this work, a photoelectrochemical sensor for Cd²⁺ composed of Au/ZnS/ZnO modified nickel foam is prepared hydrothermally and by reduction. The materials and electrochemical properties are characterized systemically. The Au/ZnS/ZnO electrode exhibits a linear relationship with Cd²⁺ concentrations in the range of 0.1 µM – 100 µM with a correlation coefficient of 0.9993 in conjunction with a high sensitivity of 158.3 µA µM⁻¹ cm⁻². The synergistic structure boosting detection of Cd²⁺ with high sensitivity and selectivity has broad application prospect in environmental science and pollution control.

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Cadmium ions (Cd²⁺) impact human health as Cd²⁺ in the body cannot be degraded consequently causing damage to human organs and the immune system. Therefore, it is imperative to detect Cd²⁺ in the environment quickly and sensitively. Different methods have been developed to detect Cd²⁺, for instance, atomic absorption spectrometry (AAS), inductively-coupled plasma atomic emission spectrometry (ICP-AES), and inductively-coupled plasma mass spectrometry (ICP-MS). Although these methods offer high accuracy, they require high-precision instruments and skilled technicians and therefore, it is urgent to develop simpler and less labor-intensive techniques.

Photoelectrochemical (PEC) analysis capitalizes on electron transfer and energy conversion during light excitation and the optical excitation signal and electrochemical detection signal can be separated. Huang et al. have reported a methylene blue (MB) sensitized PEC biosensor for sensitive Pb (II) detection and Xu et al. have described an immobilization and label-free PEC aptasensor for Hg (II) detection with the solution-phase photoactive probe (MB) and exonuclease III-assisted amplification. Owing to the different excitation signals and detection signals, PEC analysis offers the advantages of high sensitivity, rapid analysis, and reduced noise interference.

Zinc oxide (ZnO), a wide bandgap semiconductor (3.37 eV) with many unique properties such as high charge carrier mobility, is commonly used in sensors, photocatalysts, and photovoltaic devices. ZnO can produce photocurrents in PEC sensing and absorb ultraviolet light. Jiang et al. have prepared pincene ZnO/rGO with excellent photocatalytic properties for degradation of Rhodamine B. Tian et al. have reported that CuInS₂/ZnS quantum dots can detect Cd²⁺ via the displacement reaction and deposition of gold (Au) nanoparticles (NPs) can increase the conductivity and sensitivity of the electrode. In addition, ZnS can produce photocurrent in PEC sensing, produce electron transition and provide energy under ultraviolet light irradiation.

In this work, a PEC Cd²⁺ sensor comprising the Au/ZnS/ZnO electrode is designed and fabricated. ZnS reacts with Cd²⁺ to produce CdS on the surface of ZnO to generate photocurrents under ultraviolet light irradiation. Au NPs have better conductivity and introduce surface plasmonic effects to enhance the photocurrents and electron transfer. The Au/ZnS/ZnO electrode shows excellent sensitivity and selectivity including a linear relationship with Cd²⁺ concentrations in the range of 0.1 µM – 100 µM and correlation coefficient of 0.9993.

Experimental

Materials.—The nickel (Ni) foam (thickness of 1.5 mm, pore density of 100 PPI, surface density of 380 g m⁻²) was purchased from Changsha Profat New Materials Co., Ltd. and the other chemicals were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the reagents were analytical grade and used as received. The aqueous solutions were prepared with deionized water.

Preparation of ZnO on Ni foam.—The Ni foam (1 × 1 cm) was washed in deionized water, diluted hydrochloric acid, and ethanol for 15 min each to remove surface oxide and impurities. In the typical synthesis, 0.05 nmol zinc acetate dihydrate ((Zn (CH₃COO)₂·2H₂O) was dissolved in 50 ml of deionized water and sonicated for 15 min to form a homogeneous solution. The Ni foam was placed in the solution for 5 min, taken out, and annealed at 200 °C in air for 30 min to form the ZnO seed layer. 25 mM zinc nitrate hexahydrate (Zn (NO₃)₂·6H₂O) and 25 mM hexamethylenetetramine (HMTA) were dissolved in 40 ml of deionized water and sonicated. The pretreated Ni foam was transferred to the Teflon lined autoclave stainless steel containing the above solution and heated to 90 °C for 5 h. After cooling, it was washed with deionized water and dried at 60 °C for 2 h to form ZnO on nickel foam.

Preparation of ZnS/ZnO on Ni foam.—The ZnS microphases were synthesized by a hydrothermal process. 2.28 g of thiourea and 6.56 g of Zn (CH₃COO)₂·2H₂O were dissolved in 50 ml of deionized water and stirred for 40 min. The solution was transferred to a 50 ml Teflon lined stainless steel autoclave. The Ni foam and ZnO Ni foam were introduced to the solution and heated to 125 °C for 24 h. After cooling to room temperature, the products were rinsed with deionized water and ethanol and dried at 60 °C for 2 h to obtain ZnS and ZnS/ZnO.

Preparation of Au/ZnS/ZnO on Ni foam.—Au NPs synthesized by the citrate reduction method were deposited on the surface of the electrode. 0.5 ml of HAuCl₄ (1 wt%) was added to 50 ml of deionized water and stirred ultrasonically. The HAuCl₄ solution was heated to 100 °C and trisodium citrate (2.5 ml, 1 wt%) was added. When the solution underwent reduction, the color changed from pale yellow to purple and finally deep red. The solution was
cycled naturally to room temperature, sealed, and stored at 4 °C for further use. The ZnS/ZnO electrode was placed in the Au NPs solution for 3 – 5 min and the soaked Ni foam was annealed at 60 °C for 30 min to form the Au/ZnS/ZnO electrode. The above experimental steps were repeated two or three times to ensure that the Au NPs were deposited on ZnS/ZnO evenly.

**Characterization and measurements.** — The morphology of the samples were characterized by scanning electron microscopy (SEM, Hitachi S-3400, 20 kV) and transmission electron microscopy (TEM, Hitachi H-7650). The structure was determined by X-ray diffraction (XRD, D8 discovery Bruker, 40 kV, 40 Ma, Cu, Kα, λ = 1.5406 Å) and the elemental composition was determined by X-ray photoelectron spectroscopy (XPS, VG Scientific Escalab250). Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and photoelectrochemical (PEC) tests were performed on the CHI604E electrochemical workstation (China Chenhua). The three-electrode configuration consisting of the platinum electrode, Hg/HgO (saturated KCl) reference electrode, and Au/ZnS/ZnO working electrode was adopted. CV and EIS were carried out in 1 M KOH. The photocurrents were monitored by chronoamperometry (CA) and some nanorods are clustered to improve the stability of the ZnO composite shows ZnS microspheres and Au NPs on the surface. The surface roughness resulting in better ion/electron transfer between the electrode and test solution. In the Au/ZnS/ZnO composite, the ZnS microspheres can fully contact cadmium ions in the solution to form a three-dimensional network similar to that observed by SEM. The Au NPs and ZnS microspheres deposited on the ZnO nanorods form a compact spherical clusters. The Au/ZnS/ZnO becomes rough and the surface area increases to enable more contact with the test solution for better sensitivity.

Figure 1 illustrates the synthesis of Au/ZnS/ZnO on Ni foam. The ZnO seed layer is prepared on Ni foam and ZnO nanorods are deposited by annealing. The surface area increases to facilitate growth of ZnS microspheres and Au NPs. The ZnS microspheres are deposited on the ZnO nanorods by a hydrothermal method and Au NPs prepared by thermal reduction are anchored on the electrode surface. The Au/ZnS/ZnO composite is deposited on Ni foam to form the Au/ZnS/ZnO electrode.

The ZnO, ZnS, and Au/ZnS/ZnO samples are examined by SEM as shown in Fig. 2. The dense ZnO nanorods with a stable flower morphology are uniformly distributed on the Ni foam to facilitate deposition of ZnS microspheres and Au NPs. Dense ZnS microspheres with different size but similar shape are formed uniformly on the Ni foam to generate compact spherical clusters. The Au/ZnS/ZnO composite shows ZnS microspheres and Au NPs on the surface and some nanorods are clustered to improve the stability of the materials. The ZnS microspheres and Au NPs grow irregularly on the ZnO nanorods to increase both the specific surface area and surface roughness resulting in better ion/electron transfer between the electrode and test solution. In the Au/ZnS/ZnO composite, the ZnS microspheres can fully contact cadmium ions in the solution to generate a CdS/ZnO heterogeneous interface which produces photocurrents during ultraviolet light exposure. The Au NPs improve adsorption of Cd²⁺ and enhance the photocurrents upon ultraviolet light illumination to achieve better sensitivity. The ZnO, ZnS, and Au/ZnS/ZnO nanorods with similar widths and smooth edge are distributed evenly consistent with SEM and ZnS microspheres with a similar shape but different sizes are also evenly arranged. The Au NPs and ZnS microspheres deposited on the ZnO nanorods form a three-dimensional network similar to that observed by SEM. The surface of Au/ZnS/ZnO becomes rough and the surface area increases to enable more contact with the test solution for better sensitivity.

Figure 4 shows the XRD patterns of ZnO, ZnS, and Au/ZnS/ZnO on Ni foam. The (111), (200) and (220) diffraction peaks emerge from the Ni foam (Ni-JCPDS card No. 01–089–7128) at 2θ = 44.8, 52.3, and 76.1°. The black curve shows diffraction peaks at 2θ = 31.8, 34.4, 36.2, 47.5, 56.6, 62.9, 66.4, 67.8, and 69.1° related to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes of ZnO (JCPDS card No. 36–1451). The red curve shows diffraction peaks at 2θ = 28.6, 48.2, and 57.3° stemming from the (111), (220), and (311) planes of ZnS (JCPDS card No. 05–0566). The ZnS microspheres can fully contact cadmium ions in the solution to form a three-dimensional network similar to that observed by SEM. The surface of Au/ZnS/ZnO becomes rough and the surface area increases to enable more contact with the test solution for better sensitivity.

Figure 3 depicts the TEM images of ZnO, ZnS, and Au/ZnS/ZnO on Ni foam. The (111), (200) and (220) diffraction peaks emerge from the Ni foam (Ni-JCPDS card No. 01–089–7128) at 2θ = 44.8, 52.3, and 76.1°. The black curve shows diffraction peaks at 2θ = 31.8, 34.4, 36.2, 47.5, 56.6, 62.9, 66.4, 67.8, and 69.1° related to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes of ZnO (JCPDS card No. 36–1451). The red curve shows diffraction peaks at 2θ = 28.6, 48.2, and 57.3° stemming from the (111), (220), and (311) planes of ZnS (JCPDS card No. 05–0566). The ZnS microspheres can fully contact cadmium ions in the solution to form a three-dimensional network similar to that observed by SEM. The surface of Au/ZnS/ZnO becomes rough and the surface area increases to enable more contact with the test solution for better sensitivity.

Figure 5 calibrates the C 1 s peak at 284.8 eV reveal the presence of C, Zn, Au, and S. As shown in Fig. 5b, the Zn 2P₃/₂ and Zn 2P₁/₂ peaks appear at 1021.3 and 1044.4 eV and the gap of 23.1 eV indicates Zn²⁺. The XPS spectra in Fig. 5 calibrated to the C 1 s peak at 284.8 eV reveal the presence of C, Zn, Au, O, and S. As shown in Fig. 5b, the Zn 2P₃/₂ and Zn 2P₁/₂ peaks appear at 1021.3 and 1044.4 eV and the gap of 23.1 eV indicates Zn²⁺. The ZnO peaks are at 350.4 and 351.7 eV. The O₂⁻ peak at 530.4 eV is related to hydroxyl groups and the O₂⁺ peak at 530.4 eV is associated with O in ZnO. The XPS spectra in Fig. 5 calibrated to the C 1 s peak at 284.8 eV reveal the presence of C, Zn, Au, O, and S. As shown in Fig. 5b, the Zn 2P₃/₂ and Zn 2P₁/₂ peaks appear at 1021.3 and 1044.4 eV and the gap of 23.1 eV indicates Zn²⁺. The ZnO peaks are at 350.4 and 351.7 eV. The O₂⁻ peak at 530.4 eV is related to hydroxyl groups and the O₂⁺ peak at 530.4 eV is associated with O in ZnO. The XPS spectra in Fig. 5 calibrated to the C 1 s peak at 284.8 eV reveal the presence of C, Zn, Au, O, and S. As shown in Fig. 5b, the Zn 2P₃/₂ and Zn 2P₁/₂ peaks appear at 1021.3 and 1044.4 eV and the gap of 23.1 eV indicates Zn²⁺. The ZnO peaks are at 350.4 and 351.7 eV. The O₂⁻ peak at 530.4 eV is related to hydroxyl groups and the O₂⁺ peak at 530.4 eV is associated with O in ZnO.
When the Au/ZnS/ZnO electrode is exposed to ultraviolet light, the oxidation peak and reduction peak currents increase, indicating that the electrode is sensitive to ultraviolet light and the ZnO nanorods and Au NPs enhance the photoelectric effects. The oxidation peak and reduction peak currents of Au/ZnS/ZnO in the 1 μM Cd²⁺ solution increase indicating that the electrode is more sensitive to Cd²⁺. The replacement reaction between the active substance and Cd²⁺ on the electrode surface is responsible for the increase. Upon ultraviolet light exposure, the Au/ZnS/ZnO electrode in the 1 μM Cd²⁺ solution shows more intense oxidation and reduction peaks because adsorption of Cd²⁺ and photoelectric effects are promoted. Figure 6b shows the CV curves of Au/ZnS/ZnO in solutions with different Cd²⁺ concentrations upon irradiation with ultraviolet light.

With increasing Cd²⁺ concentrations, the oxidation peak currents increase gradually because more species participate in the replacement reaction. Cd²⁺ in the electrolyte enhances the positive shift in the oxidation peak potential and provides clues that the Au/ZnS/ZnO electrode can detect Cd²⁺ sensitively.

EIS is carried out to analyze the charge transfer characteristics. A 5 mV AC perturbation is introduced in the frequency range from 0.01 Hz to 100 kHz in the open circuit potential. Figure 7 shows the Nyquist diagrams of ZnO, ZnS, ZnS/ZnO, and Au/ZnS/ZnO. They are composed of semicircles in the high frequency region and inclined straight lines in the low frequency region. They are fitted by the EIS data and the equivalent circuit model is presented in Fig. 7. The ZnO electrode has a high electron transfer rate and becomes a
high-performance electron acceptor. After ZnS is deposited on ZnO, ZnS hinders electron transfer between the electrode and electrolyte and increases the transfer resistance of ZnS/ZnO. Au NPs have excellent conductivity and improve the electron transfer rate to

Figure 4. XRD patterns of ZnO, ZnS, and Au/ZnS/ZnO.

Figure 5. XPS spectra: (a) Au/ZnS/ZnO, (b) Zn 2p, (c) Au 4f, (d) O 1s, and (e) S 2p; (f) Nitrogen adsorption/desorption isotherm of Au/ZnS/ZnO with the inset showing the pore diameter distribution.

Figure 6. (a) CV curves acquired at a scanning rate of 50 mVs$^{-1}$ from the pure solution, irradiated with ultraviolet light only, with cadmium ions only, and irradiated with ultraviolet light after addition of Cd$^{2+}$; (b) CV curves of the Au/ZnS/ZnO electrode after ultraviolet irradiation in the presence of different concentrations of Cd$^{2+}$ acquired at a scanning rate of 50 mVs$^{-1}$.

Figure 7. Nyquist plots of ZnO, ZnS, ZnS/ZnO, and Au/ZnS/ZnO in 1 M KOH in the frequency range between 100 kHz and 0.01 Hz.

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reduce the interface resistance and charge transfer resistance. The semicircle of Au/ZnS/ZnO in the high frequency region is smaller than that of ZnS and ZnS/ZnO, suggesting that the electrolyte has better conductivity and lower volume resistance and contact resistance. The intercept between the Nyquist curve and real axis is the series resistance (Rs) and the series resistance of Au/ZnS/ZnO electrode is 1.6 Ω, which is much smaller than those of ZnS/ZnO (1.93 Ω) and ZnS (3.4 Ω). The linear component in the low frequency region of Au/ZnS/ZnO is related to the Warburg impedance (Zw). There is a straight line in the low frequency region and the slope is inversely proportional to the resistance, indicating lower diffusion resistance of the electrolyte to the electrode surface. All in all, the Au/ZnS/ZnO electrode shows the best electron transfer and charge transfer kinetics.

In order to further study the sensitivity to Cd$^{2+}$ under ultraviolet light irradiation, chronoamperometry (CA) is performed on the electrochemical workstation. The photocurrents of Au/ZnS/ZnO are measured at a bias potential of 0.2 V. As shown in Fig. 8a, Au/ZnS/ZnO produces photocurrents in response to different Cd$^{2+}$ concentrations and the currents increase with Cd$^{2+}$ concentrations linearly in the range between 0.1 μM and 100 μM as shown in Fig. 8b. The empirical fit is \( I = 0.1583 \, \text{C} + 4.99 \times 10^{-4} \, \text{cm}^{-2} \) with a linear correlation coefficient \( R^2 \) of 0.9993. The sensitivity is 158.3 μA mM$^{-1}$ cm$^{-2}$ and the detection limit is 0.02 μM corresponding to a signal-to-noise ratio of S/N = 3.

To assess the practical potential, the stability of Au/ZnS/ZnO is evaluated by CA. The samples is not exposed to ultraviolet light for 20 s and irradiated by ultraviolet light for 20 s. Figure 8c shows the photocurrents of Au/ZnS/ZnO for 12 exposure cycles. The photocurrent change is not obvious and relatively stable with a relative standard deviation (RSD) of 0.43%. As shown in Fig. 8d, under the same experimental conditions, the photocurrents are measured every 6 days to verify the long-term stability and after one month, 93.5% of the initial current is retained to corroborate the good stability.

The detection ranges and detection limits for Cd$^{2+}$ of the Au/ZnS/ZnO electrode and other electrodes recently reported in the literature are compared in Table I. The detection range of Au/ZnS/ZnO is larger than that of other materials and the detection limit is also lower than that of most of the other electrodes. The excellent performance of Au/ZnS/ZnO can be attributed to two factors. Firstly, effective separation of the optical excitation source and electrochemical signal eliminates interference from each other. Secondly, Cd$^{2+}$ reacts with ZnS on the surface to produce CdS and the combination of CdS and ZnO produces better photocurrent effects under ultraviolet irradiation. The synergistic effects rendered by the Au NPs also improve the sensitivity and detection range.

The selectivity and specificity for detection of Cd$^{2+}$ are important parameters in practice. In this respect, solutions with 1 μM concentration of different metals (Cd$^{2+}$, Na$^+$, K$^+$, Co$^{2+}$, Ni$^{2+}$, Fe$^{3+}$, Zn$^{2+}$, Cu$^{2+}$) are prepared for the comparative experiments in which the different photocurrents are monitored. As shown in Fig. 9a, when the Au/ZnS/ZnO electrode is irradiated with ultraviolet light in a solution with Cd$^{2+}$, significant photocurrents are observed. To determine the selectivity, different interfering metallic ions are added to the solution and no obvious change and fluctuation are observed. Figure 9b shows the photocurrents generated by Au/ZnS/ZnO during ultraviolet light exposure. In spite of the presence of interfering ions, Au/ZnS/ZnO produces large photocurrents in response to Cd$^{2+}$ but small photocurrents from other metallic ions. The results show that Au/ZnS/ZnO is more sensitive to Cd$^{2+}$ than the interfering ions.

The mechanism of PEC detection of Cd$^{2+}$ by Au/ZnS/ZnO is presented in Fig. 10. The ZnS microspheres and Au NPs on ZnO nanorods form a three-dimensional structure with a large surface area and the ZnS microspheres make full contact with the solution to improve photoelectron transfer. During light illumination, the surface plasmonic effects of Au NPs result in photoelectric energy conversion and transfer to improve the PEC efficiency. In the solution, the solubility product of CdS (\( K_{\text{sp}} = 8 \times 10^{-28} \)) is lower than that of ZnS (\( K_{\text{sp}} = 1.6 \times 10^{-25} \)). When there are Cd$^{2+}$ ions in the solution, the electrode surface of the Cd$^{2+}$ ions sensor will undergo displacement reaction, resulting in the formation of hybrid CdS.

Figure 8. (a) Photocurrents of Au/ZnS/ZnO in the presence of different concentrations of Cd$^{2+}$; (b) Linear relationship between the photocurrents and Cd$^{2+}$ concentrations; (c) Time-based photocurrent response of Au/ZnS/ZnO under repeated irradiation every 10 s; (d) Relationship between the photocurrents and time of Au/ZnS/ZnO.
material on the electrode surface. Because the solubility product of CdS is lower than that of ZnS, when there is Cd$^{2+}$ ions in the solution, the competitive binding effect leads to the formation of CdS on the surface of ZnO. Because the solubility of CdS is lower than that of ZnS, the competitive binding effect leads to the formation of CdS on the surface of ZnS. CdS/ZnO hybrid material generated on the electrode surface of Cd$^{2+}$ ions sensor has excellent light scattering ability, excellent charge separation and better carrier transfer characteristics. Therefore, CdS/ZnO hybrid material can significantly enhance the photocurrent intensity and is an ideal doping material for PEC applications. It is noteworthy that the plasma effect of Au NPs has significantly improved the light scattering activity of CdS/ZnO hybrid materials under light conditions. Therefore, CdS/ZnO has excellent matching band arrangement under ultraviolet irradiation. Owing to effective matching of the energy levels between ZnO and CdS, the photogenerated electrons generated by CdS are easily transferred from the conduction band to the ZnO surface and then to the conduction band of ZnO. This energy band structure is formed between ZnO and CdS and at the same time, ZnO nanorods have high electron mobility, giving rise to enhanced transmission efficiency of photogenerated carriers and photocurrents.

### Table I. Comparison between the Cd$^{2+}$ detection method described in this paper and other reported methods.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Linear range ($\mu$M)</th>
<th>LOD ($\mu$M)</th>
<th>References</th>
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<td>Au NCs</td>
<td>0.05–35</td>
<td>0.01225</td>
<td>18</td>
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<tr>
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### Conclusions

A simple and high-performance Au/ZnS/ZnO photoelectrochemical detector for Cd$^{2+}$ is designed and demonstrated. The detection has high sensitivity, reliable stability, and high selectivity for the detection of Cd$^{2+}$. The linear detection range spans from 0.1 $\mu$M to 100 $\mu$M with a correlation coefficient of 0.9993 and the sensitivity is 158.3 $\mu$A mM$^{-1}$ cm$^{-2}$. The sensor takes advantage of separation of
the optical excitation signal and electrochemical detection signal and the synergistic effects of Au NPs improve the photocurrents during ultraviolet light irradiation. The Au/ZnS/ZnO electrode with excellent properties have large practical potential as a rapid, cost-effective, and sensitive detector for Cd$^{2+}$ in environmental monitoring.

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