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To cite this article before publication: Cui Ye *et al* 2021 *Nanotechnology* in press <https://doi.org/10.1088/1361-6528/ac1094>

Manuscript version: Accepted Manuscript

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Ultrasensitive Photoelectrochemical Platform with Micro-emulsion-based p-type Hollow Silver Iodide Enabled by Low Solubility Product (K_{sp}) for H_2S Sensing

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Received xxxxxx

Accepted for publication xxxxxx

Published xxxxxx

Abstract

Since visible light accounting for massive solar radiation energy, a large amount of attention has been paid to the development of highly efficient visible-light-driven (VLD) semiconductor materials. However, despite recent efforts to construct visible light (VL) active material, hollow structure-based silver iodide (AgI) with appropriate band gap and a large surface area are limited because of lack of a proper synthesis method. Herein, hollow AgI with p-type semiconductor behavior is constructed on the basis of micro-emulsion strategy, which enables admirable cathode photoelectrochemical (PEC) response. The as-prepared hollow AgI is applied to fabricate the PEC sensing platform and reveals a low limit of detection of 0.04 fM and a wide dynamic range up to 5 orders of magnitude toward H_2S . The PEC sensing mechanism is supposed to the “signal-off” pattern on account of the ultralow solubility product (K_{sp}) of Ag_2S , derived from the precipitation reaction due to the high affinity between sulfide ion and Ag^+ . Besides, the hollow structure of AgI provides sufficient surface area for *in situ* producing Ag_2S that serves as recombination center of carrier, thus causing the efficient quenching of photocurrent signals. This work broadens the horizon of structuring VLD semiconductor nanomaterials and K_{sp} -based H_2S sensing.

Keywords: Micro-emulsion, Hollow Silver Iodide, Cathode Photoelectrochemical, Solubility Product K_{sp} , H_2S Sensing

1. Introduction

Hydrogen sulfide (H_2S), mostly derived from waste treatment and fuel burning of industrial manufacturing, has been widely concerned and studied, since it brings irreversible destruction to human health [1-6]. From the point

of view, it is urgent to construct a reliable and ultrasensitive analysis strategy for H_2S monitoring. Photoelectrochemical (PEC) determination, integrating an irradiation source with electrochemical instrument, is a good alternative, which make it possible to miniaturize the PEC sensing platform through an electronic readout [7-9]. Compared with the conventional electrochemical detection, the low background

noise endows PEC sensing a highly sensitivity while it relies on the signal increment or decrement of photocurrent response^[10,11]. Although PEC sensing has those advantages, H₂S has high affinity to react with most of the photosensitizers that may affect the signal output of PEC sensing platform^[10,12]. To address this issue, much effort still needs to be devoted to seek applicative photoelectrode materials for the high accuracy and sensitivity for H₂S quantitative analysis.

Currently, highly efficient visible-light-driven (VLD) semiconductor nanomaterials have received extensive attentions in PEC sensing^[13,14]. Various strategies have been generally adopted to synthesize VLD-based compound, such as coupling with noble or transition metals, doping with non-metallic elements, compositing with other semiconductors and so on^[15-17]. Unfortunately, those methods are focused on extending the corresponding light absorption spectrum from the ultraviolet (UV) to visible light (VL). Little attention has been paid to seek VLD semiconductor nanomaterials with suitable band gap, and regulate their micro- or nano-structures *via* screening acceptable synthetic methods for boosting their intrinsic PEC activity^[18-20]. The distinctive plasmon resonance effect in the region of VL endows kinds of noble-metal-based plasmonic catalysts with commendable VL activity^[21,22].

Silver iodide (AgI), one of silver halides compounds, representative plasmonic catalyst, possess distinct properties including light sensitivity, semiconductor-like features, and electrical and ionic transport behaviors, which indicates their huge potentials to serve as VLD semiconductor nanomaterials for photoelectrode fabrication.^[23-25] Since constructing progressive architectures is an essential step to elevate the intrinsic activity, micro-emulsion method is applicable alternative, which is mainly based on a thermodynamically stable system, including at least two immiscible liquids^[26-28]. The micro-emulsion system enables the formation of the precisely controlled size and morphology, which especially applies to the direct and rapid reaction between a salt solution and a surfactant counterion. It is the capacity of micro-emulsion system that solubilizes and stimulates reactants into nanosize reactors, and stabilizes the resultant products *via* the protective surfactant layers^[29-32]. In this case, micro-emulsion method displays huge potential in the establishment of AgI-based semiconductor nanomaterials.

In the work, hollow AgI has been successfully synthesized on the basis of the micro-emulsion method, and it serves as VLD photocathode to further fabricate the PEC sensing platform for H₂S quantitative analysis. The "signal-off" PEC mechanism is proposed on account of the pregnant reaction, in which H₂S can react with hollow AgI to *in situ* generate Ag₂S. The mentioned reaction can occur naturally because of the much lower solubility product (K_{sp}) of Ag₂S ($K_{sp}=6.3 \times$

10^{-50}) compared with that of AgI ($K_{sp}=9.3 \times 10^{-17}$)^[10]. Additionally, the reaction has a standard equilibrium constant as high as 1.4×10^{17} ^[1], and the hollow structure of AgI ensures large surface area that induces the formation of abundant recombination center, derived from the produced Ag₂S. The as-prepared PEC platform exhibits good analytical performance for H₂S sensing, highlighted with high sensitivity, low production cost, and convenient fabrication, and it is feasible for probing H₂S in industry waste gas. This work will inspire widespread application in the K_{sp} -based PEC sensing.

2. Experimental Section

2.1. Chemicals and reagents

Silver nitrate (AgNO₃), n-butyl alcohol (C₄H₁₀O), potassium iodide (KI), isooctane (C₈H₁₈), Rhodamine B (RhB), sodium sulfide (Na₂S), and sodium dodecyl benzene sulfonate (SDBS) were purchased from Aladdin Industrial Co., Ltd. (Shanghai, China). All chemicals are analytical grade and used as received. Ultrapure water was employed in whole work with a resistivity of 18.2 MΩ cm.

2.2. Synthesis of hollow AgI

Hollow AgI preparation: Firstly, AgNO₃ aqueous solution (0.3 M, 6 mL) was added into a mixture including C₂H₅O (6 mL), C₈H₁₈ (36 mL), SDBS (3.3 g), and C₄H₁₀O (12 mL) with ultrasonication at room temperature, and then a micro-emulsion system was built after 15 min. Secondly, KI aqueous solution (0.3 M, 6 mL) was tardily dropped in the above micro-emulsion system with a microsyringe under further ultrasonic processing for 30 min. Lastly, the obtained products were alternately washed several times with ethanol and ultrapure water *via* centrifugation at 10,000 rpm for 5 min, followed by freeze drying.

2.3. Photoelectrochemical Measurements

Prior to surface modification, the glass carbon electrode (GCE) was polished thoroughly on chamois leather utilizing 0.5 and 0.05 μM alumina slurry, sonicated with anhydrous ethanol and ultrapure water, and dried by nitrogen, orderly. The well-polished bare GCE was modified with the hollow AgI dispersion (2 mg mL⁻¹, 10 μL) and evaporated in air. Freshly prepared Na₂S solutions were used as H₂S donor. Then, the modified GCE was immersed in the Na₂S aqueous solution with the concentration of 0, 0.1 fM, 1 fM, 10 fM, 100 fM, 1 pM, 10 pM, 100 pM, 1 nM, 10 nM for 20 min, followed by washed with ultrapure water to remove unreacted ions^[12]. The PEC measurement of the modified photoelectrode was executed in phosphate buffer (0.1 M, 10 mL, pH=7.0) under a visible-light irradiation at an applied potential of 0 V.

Figure 1. a) Schematic illustration for hollow AgI preparation, b) XRD pattern of hollow AgI, c, d) FESEM images, and e) Elemental mapping images by EDS of hollow AgI, f, g) TEM, and h) HRTEM images of hollow AgI (temperature colors displayed in g) to increase the visibility of the hollow structure).

3. Result and discussion

With a low solubility of AgI ($K_{sp}=9.3 \times 10^{-17}$), the AgI can be prepared directly based on the precipitation reaction in the present of Ag⁺ and I⁻ in aqueous solution. Regrettably, owing to the fleet and uncontrollable precipitation reaction, it is difficult to acquire AgI with uniform size and appropriate morphology. As expected, the micro-emulsion method blazes a new trail to reduce the rate of precipitation reaction, and then adjust the nanostructure of AgI, in which the oriented growth process and the Geometry theory could be liable for structure formation of the final product [21, 25]. As seen in Figure 1a, the micro-emulsions system is generated and stabilized with the help of surfactant. It is worth mentioning that suitable addition of surfactant can form the nano-reactor with right sizes derived from micro-emulsion system, which ensures the flawlessly oriented growth towards the unique direction for hollow AgI preparation.

Figure 1b shows the XRD pattern of hollow AgI. The peaks at 2θ values of 23.7°, 39.2° and 46.3° match well with the typical diffraction peaks of (002), (110) and (112) crystal planes of AgI, ensuring it as a typically hexagonal β-AgI phase indexed to the JCPDS No. 09-0374. Figure S1 displays the scanning electron microscopy (SEM) image of solid AgI, which is generated from the direct precipitation reaction with the chaotic and solid nanostructure, while Figure 1c, S2 show

the SEM images of hollow AgI, which is synthesized based on micro-emulsion method. Figure 1d clearly depicts the hollow nanostructure. As depicted in Figure 1e, the elements of silver and iodine are of homogeneous distribution. The detailed morphology information is further characterized by Transmission electron microscopy (TEM), as seen in Figure 1f-h. Figure 1g displays the high-resolution TEM image of hollow AgI in the temperature colors, which clearly presents the perforated structure with a hollow cavity. Besides, Figure 1h indicates that the diameter size is 1.0 μm and 600 nm in the internal and external, respectively. X-ray photoelectron spectroscopy (XPS) was used to investigate the component and state of the sample. As seen in Figure S3, the wide scan survey XPS spectrum of solid AgI verifies the existence of Ag 3d and I 3d. The peaks centered at 373.28 and 367.28 eV in Figure 2a are separately assigned to Ag 3d_{3/2} and Ag 3d_{5/2}, demonstrating the presence of Ag⁺ in the sample. Furthermore, as for the high-resolution XPS spectrum of I 3d in Figure 2b, two peaks with binding energies of 629.98 and 618.58 eV are clearly observed, and are respectively ascribed to I 3d_{3/2} and I 3d_{5/2}, which are characteristic of I⁻ in AgI [33].

It is the band gap and the conduction/valence band (CB/VB) that determine the photocatalytic property of semiconductor. As depicted in Figure 2c, the absorption edge of hollow AgI is located around 460 nm, indicating the efficient ability for absorbing visible light [34].

Figure 2. XPS spectra of a) Ag 3d, and b) I 3d, c) Absorption spectrum derived from UV-vis diffuse reflectance spectroscopy (blue line) and the corresponding band gap energy (green line), d) OCP response, e) Mott-Schottky plot at 1 kHz under dark condition, f) Transient photocurrent of the samples.

The band gap energy of a semiconductor could be estimated by the following formula:

$$\alpha h\nu = A (h\nu - E_g)^{n/2} \quad (1)$$

where α , h , ν , A , and E_g are absorption coefficient, Planck constant, light frequency, a constant and band gap, respectively. Particularly, n rests with the transition characteristics of a semiconductor, that is, $n=1$ for direct transition, and $n=4$ for indirect transition. Thus, the E_g of AgI is determined to be 2.78 eV, which results from the plot of $(h\nu)$ versus $(\alpha h\nu)^2$, and is identified with that of previously reported work [35]. In the case, the conduction band edge (E_{CB}) and the valence band edge can be calculated using the following equation:

$$E_{VB} = X - E_e - 0.5 E_g \quad (2)$$

$$E_{CB} = E_{VB} - E_g \quad (3)$$

where E_e shows the energy of free electrons at the hydrogen scale with a constant value of 4.5 eV, and X represents the absolute electronegativity ($X_{AgI} = 5.475$). The valence band edge (E_{VB}) for hollow AgI is calculated to be 2.365 eV, and the corresponding value of E_{CB} is -0.415 eV. Figure 2d depicts the open circuit potential (OCP) of hollow AgI under dark condition and visible light irradiation. The rapid OCP response is obtained along much more positive

potential under visible light irradiation. Afterwards, the OCP reduces under the dark condition. Those results indicate the photocathode signal response of hollow AgI. As seen in Figure 2e, Mott-Schottky analysis is further executed under dark condition at 1 kHz for hollow AgI. The Mott-Schottky plot displays a negative slope, which forcefully verifies the p-type semiconductor. Consequently, the hollow AgI with p-type semiconductor behavior can be served as a applicative photoelectrode materials and enable admirable cathode PEC response.

To verify the micro-emulsion method-based hollow AgI possessing superior PEC sensing property, the PEC signal of hollow and solid AgI was recorded under visible light irradiation for several on-off cycles. Figure 2f shows the photocurrent promptly increased, and then decreased as the visible light irradiation was turned on and off step by step. Besides, strong photocurrent intensity and satisfactory reproducibility are clearly observed under visible light irradiation. By comparison, solid AgI shows a much weaker photocurrent intensity (181 nA) than that of hollow AgI (310 nA), indicating the splendid separation efficiency of electron-hole pairs and much more efficient photogenerated electrons for hollow AgI.

Figure 3. The optimization of experiment conditions for the sensing with a) pH, b) incubation time, c) concentration of hollow AgI.

To acquire good H_2S sensing performance of hollow AgI-based PEC platform, the optimal conditions including pH, accumulation time, and the modification amount of hollow AgI were investigated with the help of 10 nM H_2S (Figure 3). As seen in Figure 3a, the as-developed PEC sensor platform could present highly stable PEC responses to H_2S in either the acidic or alkaline conditions, which is consistent with the reported work [12]. Figure 3b shows the decreases of photocurrent response regularly with the extending of incubation time, and there is no obvious change of the photocurrent signals after 20 min, in which 20 min is chosen as the optimal incubation time. Besides, the modification amount of hollow AgI is investigated to obtain an ideal performance of the as-prepared PEC platform of H_2S sensing. As shown in Figure 3c, the photocurrent always declines, and then levels off while the concentration of hollow AgI is 2 mg mL^{-1} . The result reveals the optimal modification amount of hollow AgI is with a concentration of 2 mg mL^{-1} .

The hollow AgI was applied as a photocathode material to construct the PEC sensing platform for H_2S detection. For the PEC sensing, the quantitative relation between the photocurrent signal and the H_2S concentrations is displayed in Figure 4a. The more the concentration augments, the lower the PEC response decreases. Figure 4b depicts a good linear relation in the dynamic range from 0.1 fM to 10 nM, in which the linear equation is $i \text{ (nA)} = 8.29 \lg c \text{ (nM)} - 105.1$ ($R^2 = 0.992$), and the low limit of detection of 0.04 fM. Noticeably, the PEC sensing platform demonstrates a superior analytical performance with a wide dynamic range up to 5 orders of magnitude, compared to most of the previously reported work, as seen in Table S1. The selectivity of as-fabricated PEC sensing is investigated, employing the potentially

competitive anions. As displayed in Figure 4c, a significant photocurrent decrease is observed only under the existence of analyte (10 nM), and the mixture with the analyte and potential interferences. In the present of 50-fold potential interferences, the sensor barely shows photocurrent decrease. The result certifies its good selectivity, which is firmly ascribed to the high affinity between the sulfide ion and Ag^+ , small K_{sp} of Ag_2S (6.3×10^{-50}), and high standard equilibrium constant (1.4×10^{17}).

As a proof-of-concept, the PEC sensing mechanism in this work is based on the rapid recombination of the photoexcited electrons and holes after transferring from the hollow AgI to Ag_2S , as depicted in Figure 4d. Notably, the reaction that AgI reacts with sulfide to *in situ* form Ag_2S on the surface of hollow AgI is spontaneous, because the K_{sp} of Ag_2S ($K_{\text{sp}} = 6.3 \times 10^{-50}$) is much lower than that of AgI ($K_{\text{sp}} = 9.3 \times 10^{-17}$), and the mentioned conversion reaction has a standard equilibrium constant as high as 1.4×10^{17} . As far as we know, the bandgap of AgI is ~ 2.78 eV with the conduction band (CB) bottom at -0.415 eV and valence band (VB) top at ~ 2.365 eV, and the bandgap of Ag_2S is ~ 1.05 eV with CB bottom at ~ 0.06 eV and VB top at ~ 0.99 eV. Obviously, the CB of AgI possesses a more negative potential than that of Ag_2S , and the VB of AgI possesses a more positive potential than that of Ag_2S . So, the photoexcited electrons and holes of AgI will be severally injected into the CB and VB of Ag_2S . That is to say, when those two are combined, the band levels do not match well. Consequently, the photoexcited carriers will be recombined in the surface of Ag_2S , and the hollow structure of micro-emulsion based AgI ensures large surface area that induces the formation of abundant recombination center, thus causing a decrease of the photocurrent signal.

Figure 4. a) PEC response, and b) corresponding calibration curve towards various H₂S concentrations of the sensing platform, c) Selectivity of the proposed PEC assay, d) PEC sensing mechanism.

To figure out the potentials of practical application, we firstly investigated the stability and repeatability of as-prepared cathode PEC platform. Figure S4 exhibits the PEC response of the prepared PEC sensor after 10 nM H₂S monitoring. After continuous PEC measurement for 10 min, the photocurrent is no obvious difference compared with the initial one, demonstrating the good stability. Besides, to evaluate the repeatability of proposed PEC sensing platform, five modified photoelectrodes were prepared for the detection of 10 nM H₂S (Figure S5). The relative standard deviations (RSD) of the recorded photocurrent response for those photoelectrodes were 3.4%, which indicating the acceptable repeatability. Subsequently, the practicability of proposed PEC sensing platform was carried out *via* the recovery tests. H₂S-containing industry waste gas was collected, and then reacted with 1.0 mM NaOH solution. The results were shown in Table S2, and the recoveries between 96.03 and 103.7% of different concentrations are obtained, certifying the fabricated PEC sensing platform has good potentials for H₂S measurement in practical samples.

Conclusion

In summary, as-prepared PEC sensing platform was developed enabled by the micro-emulsion-based hollow AgI for H₂S detection. The resultant hollow AgI as a VLD p-type semiconductor nanomaterial possesses admirable cathode PEC response. And hollow AgI-based PEC platform reveals

superior H₂S sensing performance, especially the low detection limit. It is worth mentioned that the pregnant reaction that AgI can react with sulfide to form Ag₂S with a high standard equilibrium constant. Furthermore, due to much lower K_{sp} of Ag₂S compared with AgI, “signal-off” pattern-based PEC sensing mechanism is proposed, in which hollow-structured AgI ensures sufficient surface area for *in site* generating abundant Ag₂S and serving as the recombination center of carrier. More importantly, the simple and convenient PEC sensing platform has been applied to monitoring the H₂S-containing industry waste gas. This work paces a new way toward the design of PEC analysis platform which is promising for large-scale H₂S sensing applications in environmental, biomedical and food fields.

CRedit authorship contribution statement

Cui Ye: Writing-review & editing, funding acquisition, supervision. **Fan Xu and Zhen Wu:** Writing-original draft, data curation. **ZhongFeng Gao:** Formal analysis, funding acquisition. **Minqiang Wang:** Writing - review & editing, formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21904116, 31800829), and the China Postdoctoral Science Foundation (2021M660144).

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