# Electronic Supplementary Information

# Construction of Z-scheme g-$C_3N_4$/Ag/AgI heterojunction for Highly Selective Photoelectrochemical Detection of Hydrogen Sulfide

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## 1. Experimental section

### *Chemicals and materials*

$AgNO_3$ was bought from Sinopharm Chemical Reagent Co., Ltd. $I_2$, $H_2O_2$, $HNO_3$, KCl, $KH_2PO_4$, $Na_2HPO_4$, $Na_2S \cdot 9H_2O$ and melamine were obtained from Chengdu KeLong Chemical Co., Ltd. (Chengdu, China). $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ was provided by Beijing Chemical Reagent Co. (Beijing, China).

0.1 M phosphate buffer solution (PBS) (pH 7.0) containing 0.1 M KCl, 0.1 M $KH_2PO_4$ and 0.1 M $Na_2HPO_4$ was used throughout the experiment. $[Fe(CN)_6]^{3-/4-}$ solution (pH 7.4, 5.0 mM) was prepared by dissolving $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ in PBS solution (pH 7.4). All chemicals were of analytical grade without further purification. Ultrapure water was used throughout the experiment.

### *Apparatus and characterization*

The morphologies of the prepared nanomaterials were characterized by transmission electron microscope (TEM, JEM-2100). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed with a CHI 660e electrochemistry workstation (Shanghai Chenhua Instrumission, China). During the measurement process, a three-electrode system was adopted which was comprised of a platinum wire as the counter electrode, a saturated calomel electrode (SCE, saturated KCl) as the reference electrode and a glassy carbon electrode (GCE, $\Phi$ = 4 mm) as the working electrode.





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PEC measurements were conducted with a PEC workstation (Ivium, Netherlands) and carried out in 5 mL of PBS containing electron donor $H_2O_2$ (50 μL) solution at room temperature. The excitation light source (wavelength: λ = 365 nm; radiant flux: Φ = 976 mW) was provided by a light-emitting diode (LED) lamp and switched off-on-off for 10-20-10 s and lasted 5 cycles without bias voltage.

CV measurements were performed in 2 mL of PBS solution (pH 7.0, 0.1 M) containing 5.0 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl where the potential was between -0.2 and 0.6 V at a scan rate of 50 mV/s.

EIS measurements were conducted in 2 mL of PBS (pH 7.0, 0.1 M) containing 5.0 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl over a frequency range of 10 kHz to 0.1 Hz using an alternating current potential with an amplitude of 5 mV at a direct current potential of 0.22 V.

***Preparation of g-$C_3N_4$/Ag/AgI Z-scheme heterojunction***

***Preparation of g-$C_3N_4$***

The g-$C_3N_4$ sample was synthesized according to a previously reported method. Typically, 5 g melamine in a crucible with a cover under ambient pressure in air was dried at 80 °C for 24 h, followed by calcination in a muffle furnace at 550 °C for 3 h with a heating rate of 5 °C $min^{-1}$. The prepared samples were powder-like with a light yellow color. Finally, the powders were washed with $HNO_3$ (0.1 M) and distilled water to remove any residual alkaline species (e.g. ammonia) adsorbed on the surface.

***Photo-deposition of Ag NPs on g-$C_3N_4$ surface***

The g-$C_3N_4$/Ag nanocomposite was synthesized by a photo-deposition method by using $AgNO_3$ as the precursor and PVP as a surfactant. In a typical procedure, 10 mg of the prepared g-$C_3N_4$ sample was added to 10 mL of distilled water and ultrasonically dispersed until a homogeneous suspension, followed by a magnetic stirring with the addition of 0.03 g poly-vinylpyrrolidone for 15 min. Then, 160 μL of 10 mg·mL$^{-1}$ $AgNO_3$ was added to the aforementioned solution, the percentage of Ag is 10 % compared to the added g-$C_3N_4$. Subsequently, the mixture was stirred for 10 min at room temperature and exposed to the UV light irradiation (IVIUM) for 1.5 h. The color of the suspension turned from light yellow to dark yellow due to the deposition of Ag NPs in reaction system. Finally, the obtained suspension was collected by centrifugation, washed with distilled water and ethanol alternatively for several times to remove the extra residuals and dried at 60 °C for 12 h.

***Preparation of g-$C_3N_4$/Ag/AgI Z-scheme heterojunction***

The preparation of g-$C_3N_4$/Ag/AgI was achieved by the in situ partial oxidation of g-$C_3N_4$/Ag. Specifically, the as-prepared g-$C_3N_4$/Ag dark yellow powders (5 mg) were dispersed in 5 mL distilled water to obtain a uniform suspension. Meanwhile, 10 mg of $I_2$ was dissolved in the mixture containing 1 mL of distilled water and 2 mL of ethanol to obtain a saturated solution of $I_2$. Subsequently, 50 μL of the as-prepared $I_2$ solution was added to the g-$C_3N_4$/Ag dark yellow suspension and stirred in order to partially oxidize Ag to AgI. The solution turned from brown to light purple, which suggested the in situ generation of AgI on g-$C_3N_4$/Ag surface. Eventually, the resulted suspension was collected by centrifugation, then washed with distilled water and ethanol for several times to remove the physically absorbed species and dried at 60 °C for 12 h.

### *Fabrication of PEC sensor for $H_2S$ assay*

The fabrication procedure and the function of the PEC sensor are illustrated in scheme 1. Anterior to modification, the glassy carbon electrode (GCE) was polished elaborately using α-$Al_2O_3$ powders and ultrasonically washed in deionized water and ethanol alternatively for several times until an entirely clean surface. Firstly, the GCE was modified with the as-prepared 10 μL of 0.5 mg·mL$^{-1}$ g-$C_3N_4$/Ag/AgI suspension after drying at 37 °C air oven. Secondly, $S^{2-}$ with different concentration was mixed with the same g-$C_3N_4$/Ag/AgI nanocomposite in eppendorf tube and then dropped on the cleaned GCE that was thereupon dried in 37 °C air oven. The PEC signal was apparently decreased compared to the previous photocurrent response.

## 2. Electrochemical characterizations of the PEC sensor

CV and EIS measurements were utilized to characterize the step-by-step synthesis of the Z-scheme heterojunction and the detection of $S^{2-}$. As displayed in Fig. S1, the bare GCE exhibited a pair of reversible redox peaks with an oxidation peak current of 165.4 μA. After coated with g-$C_3N_4$, the oxidation peak current decreased to 130.7 μA, suggesting the poor conductivity of g-$C_3N_4$. Nevertheless, the redox peak current was increased after Ag NPs were introduced due to effectively promoted electron transfer. The peak current was further increased to 159.3 μA after oxidation of the Ag NPs to AgI, which was attributed to the Z-scheme electron migration pathway that accelerated the transfer of charges to the electrode. Finally, the reaction of g-

$C_3N_4$/Ag/AgI with $S^{2-}$ induced a significant depression of the peak current (121.4 μA). This is due to the formation of $Ag_2S$ changed the previous Z-scheme electron transfer pathway and further decreased the charge separation efficiency. Fig. S1 shows the semicircle diameter equals electron transferresistance ($R_{et}$) of the electrode. When Ag NPs was deposited on the g-$C_3N_4$, the semicircle diameter was decreased due to the electrical conductivity of Ag NPs. After oxidation of the Ag NPs to AgI, the semicircle diameter was decreased because of the promotion of electron transfer. Ultimately, when $S^{2-}$ was added, the increased transfer resistance was observed because of the hindrance of electron transfer caused by formation of $Ag_2S$. These results strongly supported the idea that the transformation of AgI to $Ag_2S$ caused by $S^{2-}$ changed the Z-scheme electron transfer pathway of g-$C_3N_4$/Ag/AgI composite, which decreased the charge separation efficiency and further reduced the photocurrent.

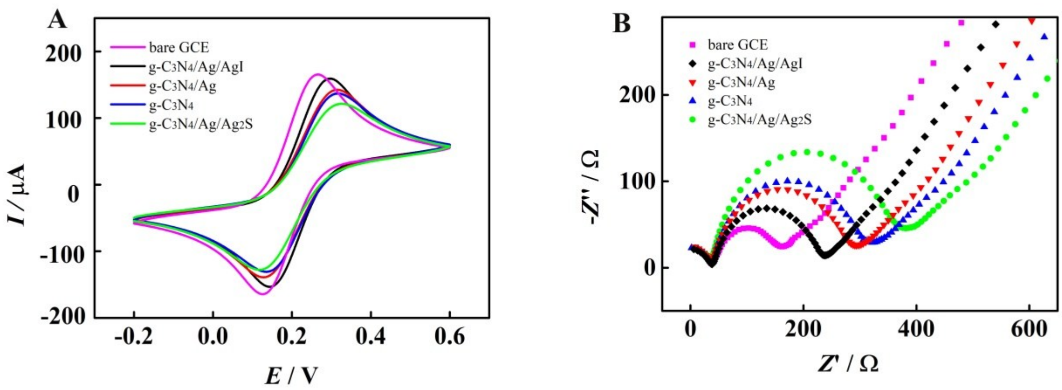


**Fig. S1** CV (A) and EIS (B) responses of the stepwise-modified electrodes: bare GCE, g-$C_3N_4$, g-$C_3N_4$/Ag, g-$C_3N_4$/Ag/AgI and g-$C_3N_4$/Ag/$Ag_2S$.

Furthermore, we also assessed the reproducibility among electrodes by comparing the

PEC response of the intra-assay and inter-assay under the same experiment conditions. The intra-assay was measured in the five same-batches of electrodes and inter assay was carried out in five different batches of electrodes in the presence of 60 μM $S^{2-}$ . As depicted in Fig. S2A, we could see that the PEC response of intra-assay variation was relatively small and the calculated RSD was 0.93 %. Meanwhile, Fig. S2B also showed small PEC response of inter-assay variation and the calculated RSD was 1.27%. Those obtained results showed that the proposed PEC strategy reflected an admirable reproducibility.

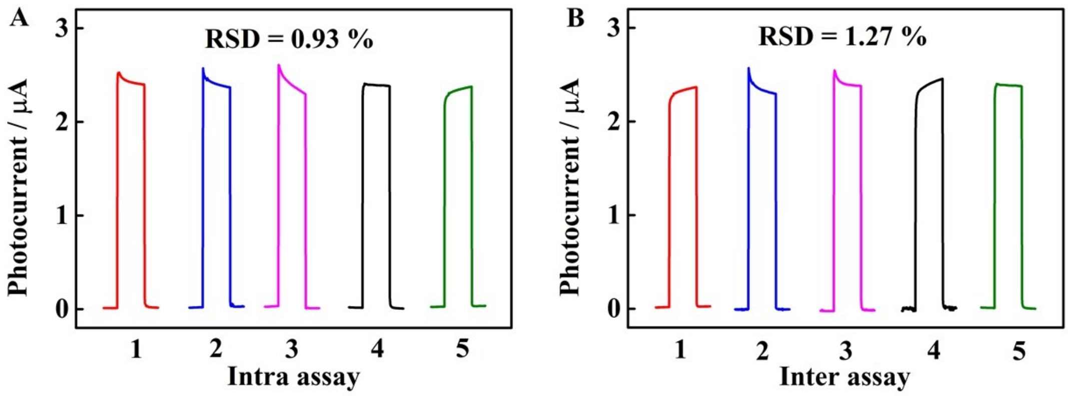


**Fig. S2** The PEC signal of intra-assay (A) and inter-assay (B) incubating with 60 μM $S^{2-}$.

***3. UV–vis, Raman spectra, XPS (X-ray photoelectron spectroscopy) characterization of g-$C_3N_4$/Ag, g-$C_3N_4$/Ag/AgI and g-$C_3N_4$/Ag/$Ag_2S$.***

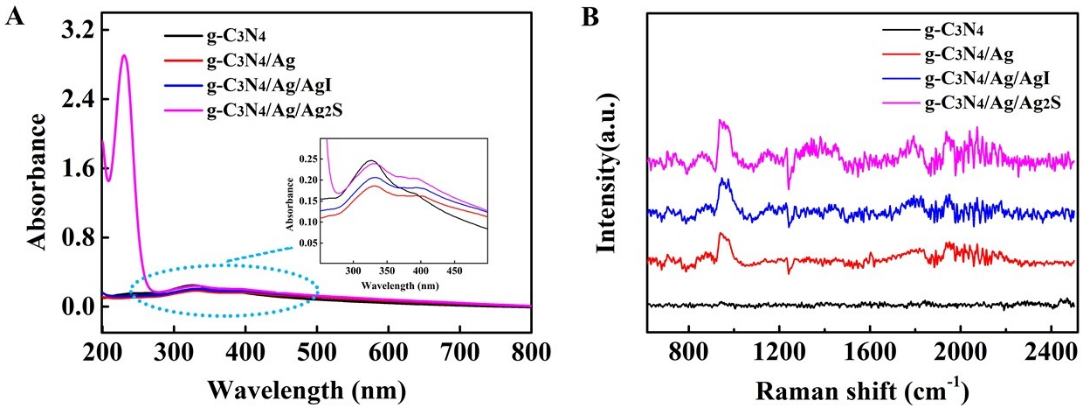


**Fig. S3** UV-vis spectra (A) and Raman spectra (B) of g-$C_3N_4$, g-$C_3N_4$/Ag, g-$C_3N_4$/Ag/AgI and g-$C_3N_4$/Ag/$Ag_2S$.

To further investigate the formation of g-$C_3N_4$/Ag, g-$C_3N_4$/Ag/AgI and g-$C_3N_4$/Ag/$Ag_2S$, XPS was characterized. High resolution XPS spectra of Ag 3d in g-$C_3N_4$/Ag, g-$C_3N_4$/Ag/AgI and g-$C_3N_4$/Ag/$Ag_2S$ were shown in Fig. S4. It can be seen that Ag 3d spectrum consists of two individual peaks, which could be ascribed to binding energies of Ag $3d_{5/2}$ and Ag $3d_{3/2}$, respectively. The binding energies of Ag 3d in g-$C_3N_4$/Ag/AgI and g-$C_3N_4$/Ag/$Ag_2S$ show negative shift in relation to that of g-$C_3N_4$/Ag. These results reveal the increase of electron density in g-$C_3N_4$/Ag/AgI and g-$C_3N_4$/Ag/$Ag_2S$, which could further confirm the formation of g-$C_3N_4$/Ag/AgI and g-$C_3N_4$/Ag/$Ag_2S$

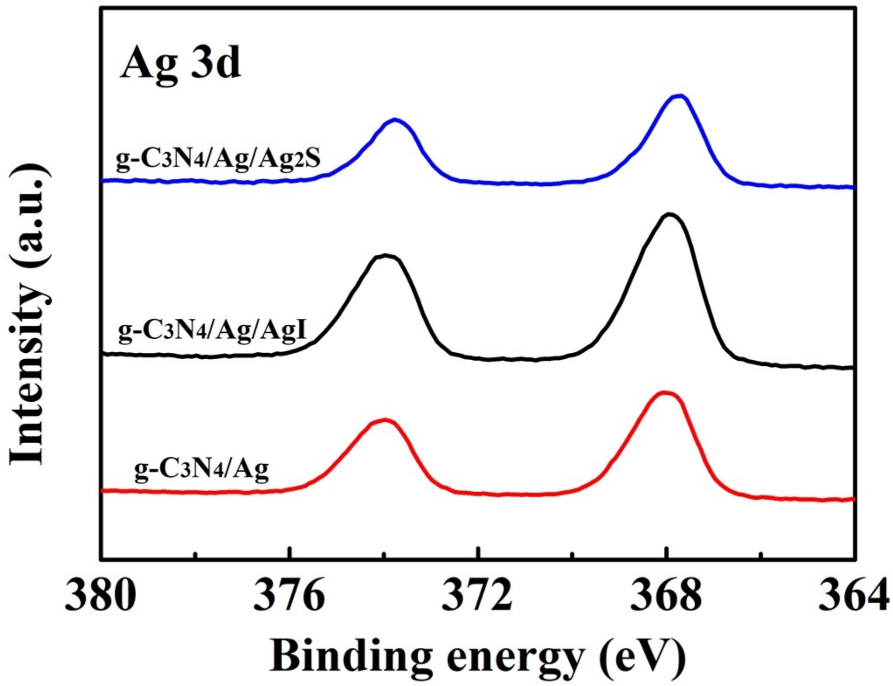


**Fig. S4** High resolution XPS spectra of Ag 3d in g-$C_3N_4$/Ag, g-$C_3N_4$/Ag/AgI and g-$C_3N_4$/Ag/$Ag_2S$.

### *3. Biocompatibility of g-$C_3N_4$/Ag/AgI heterojunction.*

To demonstrate the biocompatibility of this Z-scheme g-$C_3N_4$/Ag/AgI heterojunction, we quantified the effects of g-$C_3N_4$/Ag/AgI on the viability of CT26 cells in vitro. Cell viability was evaluated using the modified MTT assay. Fig. S5 shows the viability of CT26 cells treated with g-$C_3N_4$/Ag/AgI for 24h in media containing 0, 20, 50, 100, 200 μg $mL^{-1}$ of g-$C_3N_4$/Ag/AgI. It can be seen that g-$C_3N_4$/Ag/AgI exhibit little effects on the viability of CT26 cells over the range 0 to 200 μg $mL^{-1}$, which indicate the low toxicity of g-$C_3N_4$/Ag/AgI.

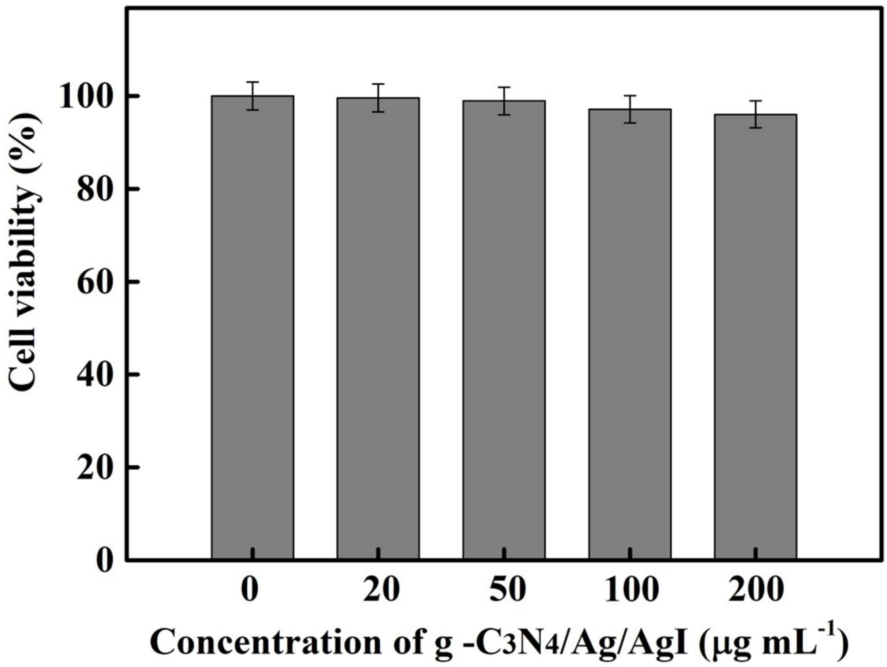


**Fig. S5** MTT assay of CT26 cells cultured for 24 h in media containing 0, 20, 50, 100, 200 μg mL$^{-1}$ of g-$C_3N_4$/Ag/AgI.





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