**In Situ Formation of Bi$_2$MoO$_6$-Bi$_2$S$_3$ Heterostructure: A Proof-Of-Concept Study for Photoelectrochemical Bioassay of L-Cysteine**

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A novel signal-increased photoelectrochemical (PEC) biosensor for L-cysteine (L-Cys) was proposed based on the Bi$_2$MoO$_6$–Bi$_2$S$_3$ heterostructure formed in situ on the indium–tin oxide (ITO) electrode. To fabricate the PEC biosensor, Bi$_2$MoO$_6$ nanoparticles were prepared by a hydrothermal method and coated on a bare ITO electrode. When L-Cys existed, Bi$_2$S$_3$ was formed in situ on the interface of the Bi$_2$MoO$_6$/ITO electrode by a chemical displacement reaction. Under the visible light irradiation, the Bi$_2$MoO$_6$–Bi$_2$S$_3$/ITO electrode exhibited evident enhancement in photocurrent response compared with the Bi$_2$MoO$_6$/ITO electrode, owing to the signal-increased sensing system and the excellent property of the formed Bi$_2$MoO$_6$–Bi$_2$S$_3$ heterostructure such as the widened light absorption range and efficient separation of photo-induced electron–hole pairs. Under the optimal conditions, the sensor for L-Cys detection has a linear range from $5.0 \times 10^{-11}$ to $1.0 \times 10^{-4}$ mol L$^{-1}$ and a detection limit of $5.0 \times 10^{-12}$ mol L$^{-1}$. The recoveries ranging from 90.0% to 110.0% for determining L-Cys in human serum samples validated the applicability of the biosensor. This strategy not only provides a method for L-Cys detection but also broadens the application of the PEC bioanalysis based on in situ formation of photoactive materials.

**Keywords:** photoelectrochemical sensor, Bi$_2$MoO$_6$–Bi$_2$S$_3$ heterostructure, L-cysteine, in situ formation reaction, ion exchange reaction
have been exploited and adopted for the PEC bioanalysis, such as steric hindrance effect (Wang et al., 2019c; Meng et al., 2020), electron donor/acceptor reaction (Li et al., 2017; Wang et al., 2019b), exciton–plasmon interactions (Ma et al., 2016; Dong et al., 2017), plasmon-enhanced effect (Li et al., 2016; Qiu et al., 2018), and in situ growth reaction (Qiu and Tang, 2020). Of these, the signaling mechanism based on the in situ growth reaction that acts directly on the electrode is not only simple to operate but also with a low background signal (Hou et al., 2016). For example, on the basis of the reaction between L-Cys and copper compounds, Zhu et al. (2017) constructed a PEC bioassay of L-Cys using a CuO–Cu2O heterojunction as a photocathode material. By using the reaction between Cu2+ and S2− from the WO3–Au–CdS nanocomposite, Zhang et al. (2019) designed a PEC immunoassay for the prostate-specific antigen. However, these works have always quantified the targets based on the signal decrease, which limits the sensitivity to some extent. By the reaction between Ag+ and BiO1/Ni electrode, Yu et al. (2019a) constructed a signal-increased biosensing system. In this system, the AgI–Ag–BiO1 Z-scheme heterojunction formed in situ greatly enhanced the PEC response, achieving satisfied detection sensitivity and stability. Considering the good performance and the few reports of such strategy, exploiting the new in situ growth reaction to construct signal-increased sensing systems and extending their applications in PEC bioanalysis are urgent and necessary.

Among various semiconductor materials, bismuth-based semiconductors possess advantages of good biocompatibility and highly visible light response (Chen et al., 2016; Zhou et al., 2017; Yu et al., 2019b). Bi2MoO6, featuring non-toxic, good stability, and adjustable morphology (Li et al., 2020), has attracted wide attention. In addition, Bi2MoO6 has a layered structure with a [Bi2O2O6]2+ layer stuck between two MoO4−2 slabs, which makes it have lots of active surfaces (Wu et al., 2018), while the PEC performance of Bi2MoO6 leaves much to be desired due to the rapid recombination between holes and electrons. In order to restrain such recombination, constructing heterostructures is one of the most effective strategies (Wang et al., 2019a; Liao et al., 2021). As a method to form heterojunctions, ion exchange can be excited by the differences in solubility of different substances and helps maintain their original state to a large extent (Wang et al., 2017). Intelligently, both Bi2MoO6 and Bi2S3 contain bismuth element, and the solubility of Bi2S3 is far less than that of Bi2MoO6. Based on this, whether the principle of the ion exchange reaction can be used for in situ generation of Bi2MoO6–Bi2S3 heterostructure and construction of a PEC biosensor?

A signal-increased PEC biosensor for L-Cys detection was proposed based on the in situ formation of a Bi2MoO6–Bi2S3 heterostructure on the indium–tin oxide (ITO) electrode. As illustrated in Scheme 1, Bi2MoO6 nanoparticles were initially coated on a bare ITO electrode. In the existence of L-Cys, Bi2S3 was generated in situ on the interface of Bi2MoO6/ITO by a chemical displacement reaction between sulfur ions from L-Cys and MoO4−2 from Bi2MoO6. The compact contact and the matchable band-edge levels of Bi2MoO6 and Bi2S3 formed a heterostructure, which broadens the light absorption range and effectively restrains the electron–hole recombination, producing an improved photocurrent response. The increased concentrations of L-Cys could generate more amount of Bi2S3 on the Bi2MoO6/ITO interface, thereby boosting the photocurrent response. By this means, a signal-increased PEC system to quantitatively detect L-Cys was established by measuring the photocurrent change of the photoelectrode.

**EXPERIMENTAL**

**Chemicals and Reagents**

Bismuth nitrate (Bi(NO3)3·5H2O), ethylene glycol (EG), and sodium molybdate (Na2MoO4·2H2O) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). t-Serine (L-Ser), glycine (Gly), and 1-tyrosine (L-Tyr) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). L-Cys and glutathione (GSH) were obtained from Aladdin Reagent Inc. (Shanghai, China). Ascorbic acid (AA), sodium sulfate (Na2SO4), and sodium sulfite (Na2SO3) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Phosphate buffer solution of 0.01 M (PBS, pH 7.4) was prepared with NaH2PO4, 2H2O, K2HPO4·3H2O, and KCl. All chemical reagents were of analytical grade, and all aqueous solutions were prepared with ultrapure water (18.2 MΩ cm).

**Apparatus**

The PEC system consists of a CHI660E electrochemical workstation (Shanghai Chenhua Apparatus Corporation, China) and a PEAC 200A PEC reaction instrument (Tianjin Aidahengsheng Science-Technology Development Co., Ltd., China). PEC experiments and linear sweep voltammetry (LSV) curves were conducted on the PEC system using a three-electrode system: an ITO electrode with a geometric area of 0.25 cm2 as the working electrode, a saturated Ag/AgCl electrode as the reference electrode, and a Pt wire as the counter electrode. The electrochemical impedance spectra (EIS) were implemented on a CHI660E electrochemical workstation in 5.0 mM K3[Fe(CN)6]/K4[Fe(CN)6] solution containing 0.1 M KCl. The scanning electron microscope (SEM) images were acquired from the Hitachi S-4800 SEM (Tokyo, Japan). UV-visible diffuse reflection spectra were recorded using a PerkinElmer Lambda 950 UV-visible spectrophotometer (United States). X-ray photoelectron spectroscopy (XPS) images were recorded on a K-Alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific Co., Waltham, MA, United States). Fourier transform infrared (FT-IR) spectra were acquired from the Bruker TENZOR 27 spectrophotometer (Bruker Optics, Germany).

**Synthesis of Bi2MoO6 Nanoparticles**

Bi2MoO6 was synthesized by a hydrothermal method (Dai et al., 2018). First, 0.4210 g of Na2MoO4·2H2O was dissolved in 5 ml of EG under stirring for 0.5 h, and 1.6866 g of Bi(NO3)3·5H2O solution was prepared in the same way. After mixing them together, 20 ml of ethanol was added dropwise under stirring. Second, the resulted solution was transferred into the Teflon-lined stainless steel
autoclave, heated to 160°C for 12 h, and cooled to room temperature. Finally, the resultant product collected by centrifugation was washed three times with ethanol as well as water, dried overnight at 80°C, and then annealed at 400°C for 3 h to obtain Bi$_2$MoO$_6$ nanoparticles.

**Fabrication of the Photoelectrochemical Biosensor**

Bi$_2$MoO$_6$ suspension of 20 microliters with a concentration of 3 mg ml$^{-1}$ was evenly dropped onto the cleaned ITO electrode and dried at 60°C for 20 min. Afterward, 20 µL of L-Cys solution was cast onto the surface of Bi$_2$MoO$_6$/ITO gently. After the reaction at 37°C for 0.5 h, the electrode was washed with water and then immersed in 0.01 M PBS (pH 7.4) containing 0.1 M AA for PEC measurement.

**RESULTS AND DISCUSSION**

**Material Characterization**

The morphology of Bi$_2$MoO$_6$ was characterized using the SEM. Figures 1A,B depicted that Bi$_2$MoO$_6$ possessed a nanosheet-assembled spherical structure, and the diameters of the microsphere were less than 3 µm. The stacked sheet structure makes the material have a large specific surface area, which benefits for the subsequent ion exchange reaction and the PEC detection. After incubated with L-Cys, parts of nanosheets granulated on the microsphere of Bi$_2$MoO$_6$ (Figure 1C), indicating the interaction between Bi$_2$MoO$_6$ and L-Cys. Additionally, the elemental mapping images in Supplementary Figure S1 suggested that Bi, Mo, O, and S elements existed in the material, indicating the reaction between Bi$_2$MoO$_6$ and L-Cys.

To characterize the chemical composition and chemical state of Bi$_2$MoO$_6$ before and after reacting with L-Cys, XPS analysis was performed. As shown in Figure 2A, the elements of Bi, Mo, and O exist in Bi$_2$MoO$_6$ samples, whereas a new element of sulfur appeared after the reaction between Bi$_2$MoO$_6$ and L-Cys. Peaks in Bi 4f spectra in Figure 2B showed that two main peaks at 159.0 and 164.3 eV belong to Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$ in Bi$_2$MoO$_6$ (Jia et al., 2018), shifted to 159.3 and 164.6 eV after the chemical reaction. This chemical shift originated from the formation of new bonds between bismuth and sulfur which changed the original chemical environment of bismuth atoms. The high-resolution XPS spectra of Mo 3d, S 2p, and O 1s of Bi$_2$MoO$_6$ after reacting with L-Cys were also conducted. The binding energy at 232.3, 235.4, 159.2, 164.4, and 531.1 eV pictured in Figures 2C–E were ascribed to Mo 3d$_{5/2}$, Mo 3d$_{3/2}$, S 2p$_{3/2}$, S 2p$_{1/2}$, and O 1s, respectively. The result further witnessed the in situ formation of Bi$_2$S$_3$ on Bi$_2$MoO$_6$ (Li et al., 2020).

The optical property of Bi$_2$MoO$_6$ before and after reacting with L-Cys was studied by FT-IR spectroscopy and UV-vis DRS. As can be seen from Figure 3A, the characteristic peak at 712 cm$^{-1}$ existed both in the FT-IR spectrum of Bi$_2$MoO$_6$ and
that after reacting with L-Cys, attributing to the symmetrical tensile vibration of the top oxygen atom of MoO$_6$$^{6-}$ (Zhang et al., 2010; Li et al., 2014a; Tian et al., 2015). Compared with the FT-IR spectrum of Bi$_2$MoO$_6$, a new peak at 842 cm$^{-1}$ appeared in the chart of Bi$_2$MoO$_6$ after the reaction with L-Cys. This new peak corresponds to the stretching vibration of Bi–S, indicative of the formation of Bi$_2$S$_3$ through the reaction between Bi$_2$MoO$_6$ and L-Cys (Zhao et al., 2017). The UV-vis DRS in Figure 3B suggested that the formation of Bi$_2$MoO$_6$–Bi$_2$S$_3$ widened the absorption range of the light irradiation and thus is benefit for the subsequent PEC analysis.

**Condition Optimizations**

As a photoactive material to construct the photoelectrode, the concentration of Bi$_2$MoO$_6$ plays a crucial effect on the PEC performance of the sensor. The photocurrent signal of the Bi$_2$MoO$_6$/ITO electrode constructed with varied concentration of Bi$_2$MoO$_6$ was recorded, and the photocurrent response reached a maximum value when the concentration of Bi$_2$MoO$_6$ was 3 mg ml$^{-1}$ (Supplementary Figure S2). So, 3 mg ml$^{-1}$ Bi$_2$MoO$_6$ was used for the subsequent experiments. In addition, the reaction time of Bi$_2$MoO$_6$ with L-Cys was optimized. According to Supplementary Figure S3, the photocurrent response gradually enhanced with the increase of reaction time, but the signal tended to stabilize when the reaction time reached 30 min. Therefore, 30 min was used as the reaction time.

**Electrochemical and Photoelectrochemical Characterizations**

To explore the interfacial electrochemical behavior of the biosensor, EIS analysis was conducted. As seen from Figure 4A, the bare ITO electrode displayed a small electron-transfer resistance ($R_\text{et}$), whereas the Bi$_2$MoO$_6$/ITO electrode gave an increased $R_\text{et}$ because the coating of the semiconductor impedes the electron transfer. After Bi$_2$MoO$_6$/ITO
was incubated with L-Cys, the $R_{ct}$ declined. This result may be because the in situ formation of $\text{Bi}_2\text{S}_3$ on the interface of $\text{Bi}_2\text{MoO}_6$/ITO improved the electrical conductivity of the electrode. The photocurrent responses of the sensor at different modification stages were also investigated. As illustrated in Figure 4B, almost no PEC response was shown on the bare ITO electrode, while an evident photocurrent response was observed when $\text{Bi}_2\text{MoO}_6$ was immobilized on the electrode. After reacting with L-Cys ($10 \mu\text{mol L}^{-1}$), the $\text{Bi}_2\text{MoO}_6$/ITO electrode gave a much stronger photocurrent response. This is because the compact heterostructure formed between $\text{Bi}_2\text{S}_3$ and $\text{Bi}_2\text{MoO}_6$ by in situ formation of $\text{Bi}_2\text{S}_3$ on $\text{Bi}_2\text{MoO}_6$ and the matchable band-edge levels of $\text{Bi}_2\text{MoO}_6$ and $\text{Bi}_2\text{S}_3$ could effectively accelerate the transfer of the photo-excited charge carriers. The valence band (VB) and conduction band (CB) energy levels of $\text{Bi}_2\text{MoO}_6$ and $\text{Bi}_2\text{S}_3$ were determined by the electrochemical method (Supplementary Figure S4), and the charge transfer in $\text{Bi}_2\text{MoO}_6$-$\text{Bi}_2\text{S}_3$ heterostructure is illustrated in Scheme 2. Under the light irradiation, the photo-generated electrons in the CB of $\text{Bi}_2\text{S}_3$ ($-0.36$ eV) easily transferred to the CB of $\text{Bi}_2\text{MoO}_6$ ($-0.17$ eV), whereas the holes in the VB of $\text{Bi}_2\text{MoO}_6$ ($2.69$ eV) moved to the VB of $\text{Bi}_2\text{S}_3$ ($1.33$ eV).

**Analytical Performance**

The PEC response of the $\text{Bi}_2\text{MoO}_6$/ITO electrode toward L-Cys was explored. As depicted in Figure 5A, the photocurrent intensity enhanced along with the increase in L-Cys concentration. The reason of this variation trend may be that more L-Cys increased the amount of $\text{Bi}_2\text{S}_3$ in situ formed on the $\text{Bi}_2\text{MoO}_6$/ITO electrode, thus facilitating the charge transfer and boosting the photocurrent enhancement. As demonstrated in Figure 5B, the photocurrent intensity of the sensor showed a linear relationship with the logarithm of L-Cys concentrations when the concentrations varied in the range of $5.0 \times 10^{-11}$–$1.0 \times 10^{-4}$ mol L$^{-1}$. The linear equation is $I = 128.7 + 8.1 \log C_{\text{L-Cys}}$ ($R^2 = 0.997$). The limit of detection is $5.0 \times 10^{-12}$ mol L$^{-1}$. Compared with some reported methods, this method demonstrates high detection sensitivity and a wide linear range for L-Cys (Table 1). The excellent performance of the sensor can be attributed to the in situ formation of $\text{Bi}_2\text{MoO}_6$-$\text{Bi}_2\text{S}_3$ heterostructure, which possesses an excellent photoelectric response under light irradiation.

**Selectivity, Reproducibility, and Stability**

The selectivity of the sensor was evaluated by testing the PEC response of $\text{Bi}_2\text{MoO}_6$/ITO toward Gly, L-Tyr, L-Lys, GSH, L-Ser, $\text{SO}_3^-$, and $\text{SO}_4^{2-}$ and the mixture of the aforementioned substances with L-Cys (all the aforementioned solutions have a concentration of $5 \mu\text{mol L}^{-1}$). As pictured in Figure 6A, the PEC responses of $\text{Bi}_2\text{MoO}_6$/ITO to Gly, L-Tyr, L-Lys, GSH, and L-Ser showed no obvious change compared with the blank solution, whereas the response of L-Cys as well as the mixture of the aforementioned interferents with L-Cys exhibited an obvious enhancement, thus demonstrating good selectivity. The reproducibility of the sensor was studied by intra-assay and inter-assay of $10 \mu\text{mol L}^{-1}$ L-Cys. The relative standard deviations (RSDs) of intra-assay by using five $\text{Bi}_2\text{MoO}_6$/ITO electrodes in the same batch and inter-assay of the electrodes in different batches were 3.0 and 4.2%, respectively, indicating good reproducibility of the sensor. In addition, the photocurrent response of $\text{Bi}_2\text{MoO}_6$/ITO for $100 \text{nmol L}^{-1}$ L-Cys within 4 weeks of storage was investigated to study the stability of the sensor. As shown in Figure 6B, the photocurrents show negligible change with RSDs less than 5.1%. The signal of this system for 15 cycles was monitored. In Supplementary Figure S5, the photocurrent
was stable with a RSD of 3.2%. The data indicate the good stability of the sensor.

**Applications**

To explore the practical application of the sensor, seven undiluted human serum samples from Xinyang Central Hospital were measured. As listed in Supplementary Table S1, compared with the reference method (enzymatic cycling) used by the hospital, the relative errors between the reference method and this method are less than 6.1%, and the RSDs are no more than 6.2%. In addition, the standard addition test results suggest that the recoveries of L-Cys are in the range of 90.0–110.0% with RSDs less than 6.8%, as shown in Supplementary Table S2. The aforementioned results show that this method has good accuracy and feasibility.

**CONCLUSION**

In summary, a facile and signal-increased PEC sensor for L-Cys detection was developed based on the *in situ* formation of Bi<sub>2</sub>MoO<sub>6</sub>–Bi<sub>2</sub>S<sub>3</sub> heterostructure. In virtue of the chemical reaction between L-Cys and Bi<sub>2</sub>MoO<sub>6</sub>, Bi<sub>2</sub>S<sub>3</sub> was formed *in situ*.
on the surface of Bi₂MoO₆, and the signal-increased sensing system endowed the sensor with high sensitivity. The Bi₂MoO₆-Bi₂S₃ heterostructure showed effective photovoltaic conversion efficiency and thus demonstrated sensitive photocurrent response under light irradiation. Thanks to the fine performance of the Bi₂MoO₆-Bi₂S₃ heterostructure, the sensor for L-Cys achieved excellent performance in sensitivity, selectivity, and stability. The proposed method based on the in situ growth reaction not only proposes a new strategy for L-Cys detection but also opens up a new perspective for PEC bioanalysis.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding authors.

**AUTHOR CONTRIBUTIONS**

H-JX: conceptualization, methodology, investigation, and writing–original draft. X-JL: investigation. HW: investigation.

**REFERENCES**

Ayaz Ahmed, K. B., Sengan, M., P., S. K., and Veerappan, A. (2016). Highly Selective Colorimetric Cysteine Sensor Based on the Formation of Cysteine Layer on Copper Nanoparticles. Sensors Actuators B: Chem. 233 (10), 431–437. doi:10.1016/j.snb.2016.04.125

Cao, J.-T., Lv, J.-L., Liao, X.-J., Ma, S.-H., and Liu, Y.-M. (2021). Photogenerated Hole-Induced Chemical-Redox Cycling Strategy on a Direct Z-Scheme Bi₂S₃/Bi₂MoO₆ Heterostructure Photocathode: Toward an Ultrasensitive Photoelectrochemical Immunosassay. Anal. Chem. 93 (28), 9920–9926. doi:10.1021/acs.analchem.0c02175

Chen, L., He, J., Liu, Y., Chen, P., Au, C.-T., and Yin, S.-F. (2016). Recent Advances in Bismuth-Containing Photoelectrocatalsys with Heterojunctions. Chin. J. Catal. 37 (6), 780–791. doi:10.1016/S1872-2067(15)61061-0

Dai, W., Hu, X., Wang, T., Xiong, W., Luo, X., and Zou, J. (2018). Hierarchical CeO₂/Bi₂MoO₆ Heterostructured Nanocomposites for Photoreduction of CO₂ into Hydrocarbons under Visible Light Irradiation. Appl. Surf. Sci. 434, 481–491. doi:10.1016/j.apsusc.2017.10.207

Deákova, Z., Dušáková, Z., Armstrong, D. W., and Lehotay, J. (2015). Two-Dimensional High Performance Liquid Chromatography for Determination of Homocysteine, Methionine and Cysteine Enantiomers in Human Serum. J. Chromatogr. A 1408, 118–124. doi:10.1016/j.chroma.2015.07.009

Dong, Y.-X., Cao, J.-T., Wang, B., Ma, S.-H., and Liu, Y.-M. (2017). Exciton-Plasmon Interactions Between CDSeeq-C₂N₄ Heterojunction and Au@Ag Nanoparticles Coupled with DNAAs-Triggered Signal Amplification: Towards Highly Sensitive Photoelectrochemical Bioanalysis of MicroRNA. ACS Sustain. Chem. Eng. 5 (11), 10840–10848. doi:10.1021/acssuschemeng.7b07274

Hou, T., Zhang, L., Sun, X., and Li, F. (2016). Biphasic Photoelectrochemical Sensing Strategy Based on In Situ Formation of CdS Quantum Dots for Highly Sensitive Detection of Acetylcholinesterase Activity and Inhibition. Biosens. Bioelectron. 75, 359–364. doi:10.1016/j.bios.2015.08.063

Huang, Z., Yang, Y., Long, Y., and Zheng, H. (2018). A Colorimetric Method for Cysteine Determination Based on the Peroxidase-Like Activity of Ficin. Anal. Methods 10 (54), 2676–2680. doi:10.1039/C8AY00707A

Jia, Y., Ma, Y., Tang, J., and Shi, W. (2018). Hierarchical Nanosheet-Based Bi₂MoO₆ Microboxes for Efficient Photocatalytic Performance. Dalton Trans. 47 (16), 5542–5547. doi:10.1039/C8DT00661A

S-WR: validation. J-TC: conceptualization, methodology, project administration, writing–original draft, and writing–review and editing. Y-ML: conceptualization, methodology, supervision, project administration, writing–original draft, and writing–review and editing.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2022.845617/full#supplementary-material

Laura Betti, L. P., Betti, L., and Giannaccini, G. (2015). Sulfur Metabolism and Sulfur-Containing Amino Acids: I-Molecular Effectors. Biochem. Pharmacol. (Los Angel) 04 (7), 1–8. doi:10.4172/2167-6501.1000158

Li, H., Liu, J., Hou, W., Du, N., Zhang, R., and Tao, X. (2014a). Synthesis and Characterization of G-3,N6,Bi₂MoO₆ Heterojunctions with Enhanced Visible Light Photocatalytic Activity. Appl. Catal. B: Environ. 160, 87–97. doi:10.1016/j.apcatb.2014.05.019

Li, J.-J., Qiao, D., Zhao, J., Weng, G.-J., Zhu, J., and Zhao, J.-W. (2019). Fluorescence Turn-On Sensing of L-Cysteine Based on FRET Between Au-Ag Nanochusters and Au Nanorods. Photochimica Acta A: Mol. Biomol. Spectrosc. 217, 247–255. doi:10.1016/j.jsa.2019.03.092

Li, J., Yang, C., Wang, W.-L., and Yan, X.-P. (2018). Functionalized Gold and Persistent Luminescence Nanoparticle-Based Ratiometric Absorption and TR-FRET Nanoplatform for High-Throughput Sequential Detection of L-Cysteine and Insulin. Nanoscale 10 (31), 14931–14937. doi:10.1039/C8NR04414G

Li, R., Yan, R., Bao, J., Tu, W., and Dai, Z. (2016). A Localized Surface Plasmon Resonance-Enhanced Photoelectrochemical Biosensing Strategy for Highly Sensitive and Sateless Cell Assay Under Red Light Excitation. Chem. Commun. 52 (79), 11799–11802. doi:10.1039/C6CC0596C

Li, R., Zhang, Y., Tu, W., and Dai, Z. (2017). Photoelectrochemical Bioanalysis Platform for Cells Monitoring Based on Dual Signal Amplification Using In Situ Generation of Electron Acceptor Coupled with Heterojunction. ACS Appl. Mater. Inter. 9 (27), 22289–22297. doi:10.1021/acsami.7b06107

Li, W., Xie, P., Chen, J., He, J., Guo, X., Yu, D., et al. (2014b). Quantitative Liquid Chromatography-Tandem Mass Spectrometry Method for Determination of Microcystin-MM and Its Glutathione and Cysteine Conjugates in Fish Plasma and Bile. J. Chromatogr. B 963, 113–118. doi:10.1016/j.jchromb.2014.05.057

Li, X., Chen, D., Li, N., Xu, Q., Li, H., He, J., et al. (2020). Efficient Reduction of Cr(Ⅵ) by a BMO/Bi₂S₃ Heterojunction via Synergistic Adsorption and Photocatalysis Under Visible Light. J. Hazard. Mater. 400, 123243. doi:10.1016/j.jhazmat.2020.123243

Liao, X.-J., Xiao, H.-J., Cao, J.-T., Ren, S.-W., and Liu, Y.-M. (2021). A Novel Split-Type Photoelectrochemical Immunosensor Based on Chemical Redox Cycling Amplification for Sensitive Detection of Cardiac Troponin I. Talanta 233, 122564. doi:10.1016/j.talanta.2021.122564

Lv, J.-L., Wang, B., Liao, X.-J., Ren, S.-W., Cao, J.-T., and Liu, Y.-M. (2021). Chemical-Chemical Redox Cycling Amplification Strategy in a Self-Powered Photoelectrochemical System: A Proof of Concept for Signal Amplified
Xiao et al. Photoelectrochemical Bioassay of L-Cysteine

Qiu, Z., Shu, J., and Tang, D. (2018). Plasmonic Resonance Enhanced Wang, B., Xu, Y.-T., Lv, J.-L., Xue, T.-Y., Ren, S.-W., Cao, J.-T., et al. (2019a). Peng, J., Huang, Q., Liu, Y., Huang, Y., Zhang, C., and Xiang, G. (2020). Wang, H., Yuan, F., Wu, X., Dong, Y., and Wang, G.-L. (2019b). Enzymatic Wu, J., Ran, P., Zhu, S., Mo, F., Wang, C., and Fu, Y. (2019). A Highly Sensitive Wu, L.-L., Wang, L.-Y., Xie, Z.-J., Zhao, F., and Zeng, B. (2019c). Z-Scheme I-BiOCl/CdS Wang, L., Tricard, S., Yue, P., Zhao, J., Fang, J., and Shen, W. (2016). Polypyrrole Wang, Q., Zhou, M., and Zhang, L. (2020). A Dual Mode Photoelectrochemical

Tian, J., Hao, P., Wei, N., Cui, H., and Liu, H. (2015). 3D Bi2MoO6 Nanosheet/TiO2 Nanobelt Heterostructure: Enhanced Photocatalytic Activities and Photoelectrochemistry Performance. ACS Catal. 5 (6), 4530–4536. doi:10.1021/acscatal.5b00560

Wang, B., Xu, Y.-T., Lv, J.-L., Xue, T.-Y., Ren, S.-W., Cao, J.-T., et al. (2019a). Ru(NH3)6+2+/Ru(NH3)63+ Mediated Redox Cycling: Toward Enhanced Triple Signal Amplification for Photoelectrochemical Immunoassay. Anal. Chem. 91 (6), 3768–3772. doi:10.1021/acs.analchem.8b05129

Wang, H., Yuan, F., Wu, X., Dong, Y., and Wang, G.-L. (2019b). Enzymatic In Situ Generation of Covalently Conjugated Electron Acceptor of PSe6 Quantum Dots for High Throughput and Versatile Photoelectrochemical Bioanalysis. Analytica Chim. Acta 1058, 1–8. doi:10.1016/j.aca.2019.01.057

Wang, H., Zhang, B., Xi, J., Zhao, F., and Zeng, B. (2019c). Z-Scheme I-BiOCl/CDs with Abundant Oxygen Vacancies as Highly Effective Cathodic Material for Photocathodic Immunosensor. Biosens. Bioelectron. 141, 111443. doi:10.1016/j.bios.2019.111443

Wang, L., Liu, Z., Wang, D., Ni, S., Han, D., Wang, W., et al. (2017). Tailoring Heterostructured Bi2MoO6/Bi2S3 Nanobelts for Highly Selective Photoelectrochemical Biocatalysis of Gallic Acid at Drug Level. Biosens. Bioelectron. 94, 107–114. doi:10.1016/j.bios.2017.02.045

Wang, L., Tricard, S., Yue, P., Zhao, J., Fang, J., and Shen, W. (2016). Polypyrrole and Graphene Quantum Dots @ Prussian Blue Hybrid Film on Graphite Felt Electrodes: Application for Amperometric Determination of L-cysteine. Biosens. Bioelectron. 77, 1112–1118. doi:10.1016/j.bios.2015.10.088

Wang, Q., Zhu, M., and Zhang, L. (2020). A Dual Mode Photoelectrochemical Sensor for Nitrobenzene and L-Cysteine Based on 3D Flower-Like Cu5S6N10S6 Double Interfacial Heterojunction Photoelectrode. J. Hazard. Mater. 382, 121026. doi:10.1016/j.jhazmat.2019.121026

Wu, J., Ran, P., Zhu, S., Mo, F., Wang, C., and Fu, Y. (2019). A Highly Sensitive Electrochemiluminescence Sensor for the Detection of L-Cysteine Based on the Rhombus-Shaped Rubrene Microsheets and Platinum Nanoparticles. Sensors Actuators B: Chem. 278, 97–102. doi:10.1016/j.snb.2018.09.066

Wu, L.-L., Wang, L.-Y., Xie, Z.-J., Pan, N., and Peng, C.-F. (2016). Colorimetric Assay of L-Cysteine Based on Peroxidase-Mimicking DNA-Ag/Pt Nanoclusters. Sensors Actuators B: Chem. 235, 110–116. doi:10.1016/j.snb.2016.05.069

Wu, Y., Song, M., Wang, Q., Wang, T., and Wang, X. (2018). A Highly Selective Conversion of Toxic Nitrobenzene to Nontoxic Aminobenzene by Cu5O4Bi/Bi2MoO6. Dalton Trans. 47 (26), 8794–8800. doi:10.1039/C8DT01536H

Yang, S., Li, G., Wang, Y., Wang, G., and Qu, L. (2016). Amperometric L-Cysteine Sensor Based on a Carbon Paste Electrode Modified with Y2O3 Nanoparticles Supported on Nitrogen-Doped Reduced Graphene Oxide. Microchim. Acta 183 (4), 1351–1357. doi:10.1007/s00604-015-1737-8

Yu, S.-Y., Mei, L.-P., Xu, Y.-T., Xue, T.-Y., Fan, G.-C., Han, D.-M., et al. (2019a). Liposome-Mediated In Situ Formation of Agl/Agl/BiO Z-Scheme Heterojunction on Foamed Nickel Electrode: A Proof-Of-Concept Study for Cathodic Liposomal Photoelectrochemical Bioanalysis. Anal. Chem. 91 (6), 3800–3804. doi:10.1021/acs.analchem.9b00352

Yu, S.-Y., Zhang, L., Zhu, L.-B., Gao, Y., Fan, G.-C., Han, D.-M., et al. (2019b). Bismuth-Containing Semiconductors for Photoelectrochemical Sensing and Biosensing. Coord. Chem. Rev. 393, 9–20. doi:10.1016/j.ccr.2019.05.008

Zhang, L., Luo, Z., Zeng, R., Zhou, Q., and Tang, D. (2019). All-Solid-State Metal-Mediated Z-Scheme Photoelectrochemical Immunoassay with Enhanced Photoexcited Charge-Separation for Monitoring of Prostate-Specific Antigen. Biosens. Bioelectron. 134, 1–7. doi:10.1016/j.bios.2019.05.052

Zhang, L., Xu, X., Zhao, X., and Zhu, Y. (2010). Controllable Synthesis of Bi2MoO6 and Effect of Morphology and Variation in Local Structure on Photocatalytic Activities. Appl. Catal. B: Environ. 98 (3–4), 138–146. doi:10.1016/j.apcatb.2010.05.022

Zhao, G., Zhang, D., Yu, J., Xie, Y., Hu, W., and Jiao, F. (2017). Multi-Walled Carbon Nanotubes Modified Bi2S3 Microspheres for Enhanced Photocatalytic Decomposition Efficiency. Ceramics Int. 43 (17), 15080–15088. doi:10.1016/j.ceramint.2017.08.036

Zhou, Q., Lin, Y., Lu, M., and Tang, D. (2017). Bismuth Ferrite-Based Photoactive Materials for the Photoelectrochemical Detection of Disease Biomarkers Coupled with Multifunctional Mesoporous Silica Nanoparticles. J. Mater. Chem. B 5 (48), 9600–9607. doi:10.1039/C7TB02354E

Zhu, J.-H., Feng, Y.-G., Wang, A.-J., Mei, L.-P., Luo, X., and Feng, J.-J. (2021). A Signal-On Photoelectrochemical Aptsensor for Chloramphenicol Assay Based on 3D Self-Supporting Agl/Agl/BiO Z-Scheme Heterojunction Arrays. Biosens. Bioelectron. 181, 113158. doi:10.1016/j.bios.2021.113158

Zhu, Y., Xu, Z., Yan, K., Zhao, H., and Zhang, J. (2017). One-Step Synthesis of CuO-Cu2O Heterojunction by Flame Spray Pyrolysis for Catholic Photoelectrochemical Sensing of L-Cysteine. ACS Appl. Mater. Inter. 9 (46), 40452–40460. doi:10.1021/acsami.7b13020

Zong, J., Yang, X., Trinchi, A., Hardin, S., and Cole, I. (2014). Carbon Dots as Fluorescent Probes for "Off-On" Detection of Cu2+ and L-Cysteine in Aqueous Solution. Biosens. Bioelectron. 51, 330–335. doi:10.1016/j.bios.2013.07.042

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