

Supplementary Material

Electrochemiluminescence biosensor for cardiac troponin I with signal amplification based on MoS₂@Cu₂O-Ag modified electrode and Ce: ZnO-NGQDs

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1. Chemicals and Materials

Ammonium tetrathiomolybdate (99.95 %) was purchased from Aladdin's Reagent (Shanghai, China). Copper nitrate trihydrate, cerous nitrate, L-cysteine, and citric acid were provided by McLean Biochemical Reagents Co. Ltd (Shanghai, China). Hydrazine hydrate was obtained from Tianjin Fuyu Fine Chemicals Co. Ltd (Tianjin, China). Trisodium citrate, sodium borohydride, and zinc nitrate were acquired from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Silver nitrate was bought from Shanghai iodine Chemical Co. Ltd (Shanghai, China). L-lysine and urea were supplied by Beijing Coupling Technology Co. Ltd (Beijing, China). The human serum sample was obtained from the local hospital. The chemical reagents used can be used without further purification. Ultrapure water (resistivity 18.25 M ω ·cm) was used throughout the experiment.

Apparatus

X-ray photoelectron spectroscopy (XPS) was acquired with Thermo ESCALAB 250XI (America). Scanning electron microscope (SEM) and energy dispersive X-Ray spectroscopy (EDX) were recorded by the JEOL JSM-6700F microscope (Japan). A common three-electrode system was employed during the experiment with a modified glassy carbon electrode (GCE, 4.0 mm in diameter) as the working electrode, and a platinum wire as the counter electrode. And Ag/AgCl (saturated KCl solution) was used as a reference electrode for ECL detection, and saturated calomel electrode (SCE, saturated KCl solution) was used as a reference electrode for electrochemical detection.

2. Experimental methods

2.1 Preparation of $\text{MoS}_2@\text{Cu}_2\text{O}$ and Ag NPs

$\text{MoS}_2@\text{Cu}_2\text{O}$ were prepared according to previous methods with a little modification [1]. Initially, 13 mg $(\text{NH}_4)_2\text{MoS}_4$ and 40 mg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in 20 mL ultrapure water and ultrasound for 25 min. Next, 100 μL $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was added to the solution with sonicating for 15 min. Then the mixed solution was transferred into a Teflon-lined stainless steel autoclave and heated at 120 °C for 10 h. After the reaction, the product was cooled to room temperature, centrifuged, and washed with ultra-pure water and anhydrous ethanol three times. Finally, the products after washing were redissolved into 3 mL of ultra-pure water for freeze-drying to obtain solid powder $\text{MoS}_2@\text{Cu}_2\text{O}$.

Ag NPs were synthesized based on previously reported literature [2]. 0.2 g $\text{C}_6\text{H}_9\text{Na}_3\text{O}_9$ was added to 95 mL ultrapure water and heated to 70 °C for a reaction for 15 min. Then 1.7 mL AgNO_3 solution (17 mg/mL) was added to the mixture. The newly conjured 2 mL NaBH_4 (1 mg/mL) was quickly added. The solution was stirred at 70 °C for 1 h. When the color of the solution turned bright yellow-brown, it indicated that silver ions were generated.

Dissolve 2 mL trisodium citrate (10 mg/mL) in 80 mL ultrapure water. The solution was then transferred to a 250 mL round-bottomed flask and heated to boiling for 15 min. Then, 10 mL of newly synthesized silver ion solution and 1.7 mL AgNO_3 solution (17 mg/mL) were added at reflux for 1 h. When the solution was golden yellow, it showed that the synthesis of Ag NPs was successful.

2.2 Preparation of Ce: ZnO

Ce: ZnO was prepared as follows [3]: first, mix 10 mL $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (6 mM) 500 μL $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (2 mM) with 1 mL L-cysteine (0.1 M). The solution was stirred continuously at 80 °C for 2 h. Then, 5 mL L-lysine (0.1 M) was added to the mixture and stirred continuously for 10 min. The mixture was then transferred to a high-pressure reaction kettle lined with Teflon and reacted at 180 °C for 12 h. Pure Ce: ZnO was obtained after cooling to room temperature and centrifugation. Finally, Ce: ZnO was redispersed into ultrapure water and stored at room temperature for subsequent experiments.

References

- [1] X. N. Zhao, Y. Li, Y. Q. Guo, Y. J. Chen, Z. Q. Su, P. P. Zhang, *Adv. Mater. Interfaces*, 2016, 3, 1600658-1600665.
- [2] Y. G. Wang, Y. L. Wang, D. Wu, H. M. Ma, Y. Zhang, D. W. Fan, X. H. Pang, B. Du, Q. Wei, *Sens. Actuators B Chem.*, 2018, 255, 125-132.
- [3] J. X. Wang, Y. Zhuo, Y. Zhou, H. J. Wang, R. Yuan, Y. Q. Chai, *ACS Appl. Mater. Interfaces*, 2016, 8, 12968-12975.