Supplementary Material

ZnCdS enhanced g-C_3N_4 electrochemiluminescence behavior based on $Rh_{0.6}Ru_{0.4}$@Ag quenching for neuron-specific enolase detection

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1. Apparatus

The morphologies and sizes of as-prepared nanomaterials were characterized by scanning electron microscope (SEM, Gemini300, Germany) and transmission electron microscope (TEM, JEM-1400, Japan). X-ray powder diffraction (XRD) patterns were acquired with a D8 advance X-ray diffractometer (Bruker AXS, Germany). The UV-vis absorption spectra were acquired by the UV-vis spectrophotometer (UV-2450, Shimadzu, Japan). Besides, the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were realized with an electrochemical workstation (Zahner Zennium PP211, Germany). And the ECL signals were monitored by the MPI-E Electrochemiluminescence Analyzer (Xi'an remax Electronic Science Tech. Co. Ltd., Xi'an China).

2. Preparation of g-C_3N_4/ZnCdS

g-C_3N_4 was synthesized according to literature reports[1]. In brief, 5.0 g of white melamine powder was placed into a covered ceramic crucible and heated at 550 ℃ for 4 h in a muffle furnace. After naturally cooling to room temperature, the yellow g-C_3N_4 product was ground to powder for further use. Then, 1 g of g-C_3N_4 powder was put into 100 mL 5 M HNO_3 solution and refluxed for 24 h at 125 ℃. After naturally cooling to room temperature, the refluxed product was centrifuged and washed with ultrapure water until pH reached 7. The final product was vacuum dried at 35 ℃ for 12 h to obtain carboxylated g-C_3N_4.

ZnCdS was prepared by hydrothermal synthesis[2]: In brief, 5 mmol $Zn(AC)_2 \cdot 2H_2O$, 5 mmol Cd $(NO_3)_2 \cdot 4H_2O$ and 1 mL ammonia water was dissolved in 20 mL water. Then, 5 mL MHP was slowly added dropwise, and the mixture was ultrasonicated for 30 min. Meanwhile, 8 mL of aqueous solution containing 10 mM NaS was prepared, which was dripped into the solution, and continuously stirred for 1 h (the solution turned yellow). The mixture was transferred to a 50 mL reaction kettle, calcined at 120 °C for 8 h. The product was washed with distilled water and absolute ethanol for 3 times, and dried in a vacuum drying oven at 90 °C for 12 h. Finally, the product is naturally cooled to room temperature.

1.5 mg g-C_3N_4 and 1.5mg ZnCdS were weighed and dissolved in EDC-NHS (1

mL) solution. After 5 h of shaking, the product was washed with ultrapure water for 3 times.

3. Preparation of Ag NPs

In a typical synthesis, 13.2 mM $AgNO_3$ solution was added into 200 mL ultrapure water, then 40 mL aqueous solution containing 90 mg trisodium citrate and 10 mL of 7.35 mM tannic acid was prepared. Under vigorous stirring at 60 ℃, the mixture is uniformly mixed. The resultant Ag NPs were cleaned by twice centrifugation of 8000 rpm for 10 min to eliminate the reducing agent and re-dispersed in ultrapure 10 mL water.

4. ECL detection of NSE

10 mL of PBS (pH 7.4) containing 0.1 M KCl and 80 mM $K_2S_2O_8$ were added to the ECL cell. The scanning potential was -1.6 - 0 V and the photomultiplier tube (PMT) was set at 450 V. The scan rate is 0.1 V/s. Then the modified electrode was placed in the ECL cell and measured the ECL signal.

5. Characterization

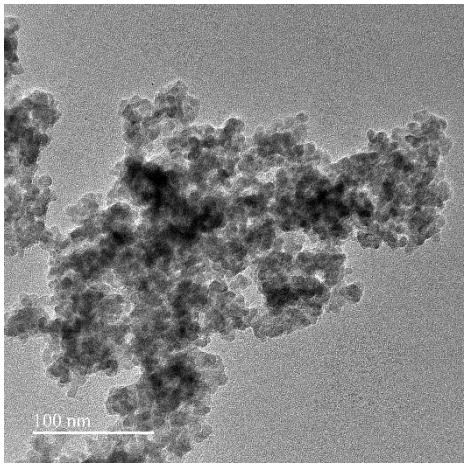

Fig.S1 HRTEM image of ZnCdS.

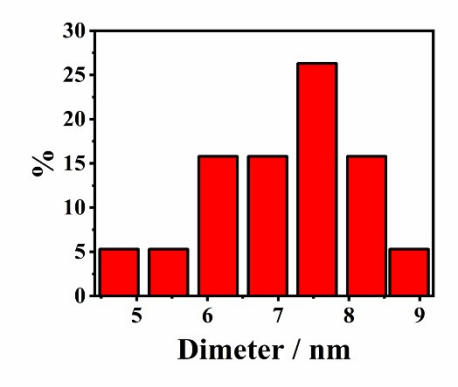

Fig.S2 Particle size analysis diagram of ZnCdS.

Reference

1. X. Li, X. Zhang, H. Ma, D. Wu, Y. Zhang, B. Du, and Q. Wei, *Biosens. Bioelectron.*, 2014, **55**, 330-336.
2. Z. Jiang, Y. Lei, M. Zhang, Z. Zhang, and Z. Ouyang, *Journal of Nanomaterials*, 2019, **2019**, 9.