

Supplementary Information

MoS₂ nanosheets grown on bowl-shaped hollow carbon spheres as an efficient electrochemical sensor for ultrasensitive determination of nephrotoxic aristolochic acids in Chinese traditional herbs

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S1. Reagents and instrument

Aristolochic acid and resorcinol were purchased from Macklin (Shanghai, China). Tetraethyl orthosilicate (TEOS) and ethanol were obtained from Aladdin (Shanghai, China). Formaldehyde was acquired from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Hydrofluoric acid (HF) and ammonium hydroxide solutions were purchased from Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. (Shanghai, China). Ammonium tetrathiomolybdate and thiourea were purchased from Rhawn (Shanghai, China). The 0.1 M phosphate-buffered saline (PBS; Na_2HPO_4 , NaH_2PO_4 , and NaCl , pH 7.0) solution was used as the electrolyte. Ultrapure water was used to prepare all solutions, and all chemical reagents used were analytically pure and were used as received, without further modification.

The X-ray diffraction (XRD) using the Ultima-IV apparatus (Rigaku, Japan). The morphology and microstructure were analyzed using scanning electron microscopy (SEM, Zeiss Sigma 300) and transmission electron microscopy (TEM, FEI Talos F200s). Valence states of surface elements and semi-quantitative analysis of those groups were determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha), and the peak of C1s at 284.8 eV was used as a blank to correct the spectrum.

Electrochemical analysis was conducted using a CHI-660E electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd., Shanghai, China) at 25 °C. Electrochemical impedance spectroscopy (EIS) experiments were performed using a Multi Autolab M204 electrochemical workstation (Metrohm Ltd., Switzerland). Linear scanning voltammetry (LSV) and EIS tests were performed using a three-electrode system comprising a Pt wire, an Ag/AgCl

electrode, and a MoS₂-BHCs-modified GCE or GCE as the counter, reference, and working electrodes, respectively.

S2. Preparation of MoS₂–BHCs/GCE

The GCE (Inner core diameter: 3mm) was polished with alumina powder (0.5 μm) on a chamois cloth to achieve a mirror-like electrode surface. The electrodes were sonicated with ultrapure water and ethanol for 10 s each, blown dry with Ar gas, and allowed to rest. *N, N*-dimethylformamide (DMF) was diluted with an equal volume of water, and then, different amounts of MoS₂–BHCs were added to 1 mL of dispersion solution. The mixtures were sonicated for 30 min to obtain well-formed dispersions. The dispersion was dropped vertically onto the electrode surface and dried naturally to obtain the MoS₂–BHCs/GCE. BHC/GCE and MoS₂/GCE were obtained by the same method. The concentration of modification was 1 mg/mL for all materials in the electrochemical characterization part of the experiment. The concentration of modification in the optimization experiment was 0.5/1/1.5/2/3 mg/mL. The optimal condition was 1 mg/mL. The volume of dispersion on the electrode in all experiments was 5 μL.

S3. Electrochemical measurements

The EIS and CV tests of the modified and the bare GCE were performed using a 0.1 mol/L KCl solution containing 0.5 mmol/L $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as the electrolyte. The salt bridge solution inside the Ag/AgCl reference electrode is a 3.5 mol/L KCl solution. A three-electrode system was used to perform LSV experiments in the potential range of -0.3 to -0.9 V and potential scan rate range of 10 - 250 mVs^{-1} . The current response of different electrodes to AAs was determined using SWV in the potential range of -0.3 to -0.9 V, at the amplitude of 25 mV, and a frequency of 25 Hz. Pre-deposition using amperometric i - t curves. The deposition conditions for the amperometric i - t curve are a deposition potential of 0 V and a deposition time of 50 s.¹ The electrolyte was flushed with Ar gas for 20 min to remove dissolved oxygen before the experiments. All experiments were conducted at 25 °C.

S4. MoS₂-BHCs characterization

The crystal structures of MoS₂-BHCs was determined by X-ray diffraction (XRD) using a Ultima-IV apparatus (Rigaku, Japan). The morphology and microstructure of MoS₂-BHCs were analyzed using scanning electron microscopy (SEM, JSM-7800F) and transmission electron microscopy (TEM, FEI Talos F200s). Valence states of surface elements and semi-quantitative analysis of those groups were determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha), and the peak of C1s at 284.8 eV was used as a blank to correct the spectrum.

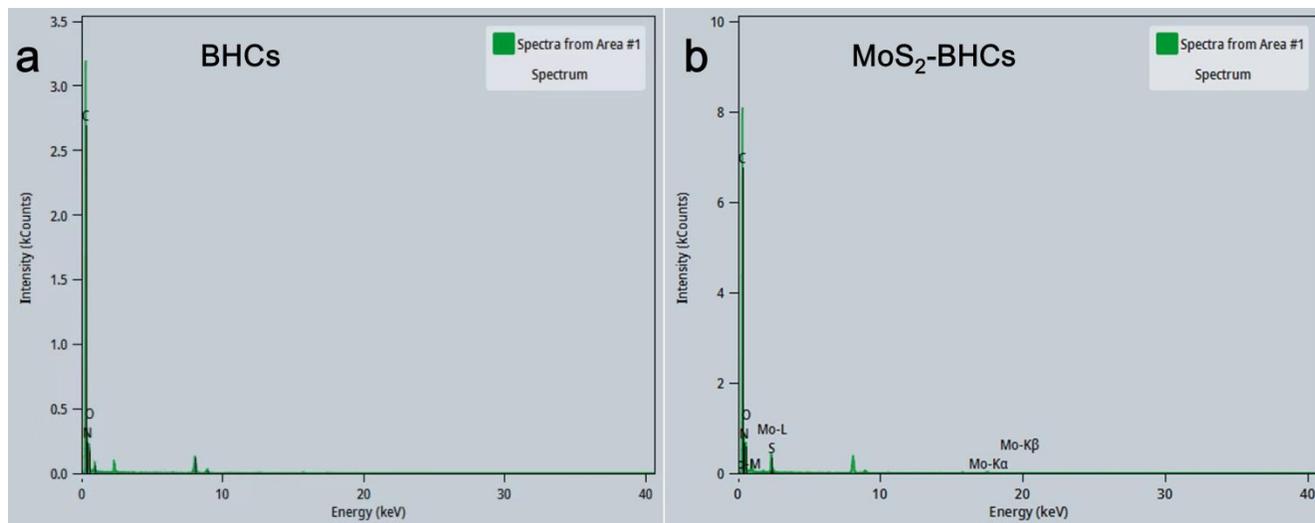


Fig S1 The EDS element distribution (a) BHCs and (b) MoS₂-BHCs

S5. Randles–Ševčíck equation

According to the Randles–Ševčíck equation, the effective surface area of the electrode can be calculated as follows:

$$I_{pa} = (2.69 \times 10^5)n^{3/2}AD^{1/2}\nu^{1/2}c$$

where I_{pa} is the peak current; n is the number of electrons transferred ($n = 1$), A is the effective surface area of the electrode, D is the diffusion coefficient ($7.6 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$), ν is the scan rate (Vs^{-1}), and c is the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ concentration (mol/cm^3). In summary, the higher conductivity, current response to AAs, electrochemical performance, and effective surface area of the MoS_2 –BHCs/GCE were higher, stronger, superior, and larger, respectively, than those of the GCE.

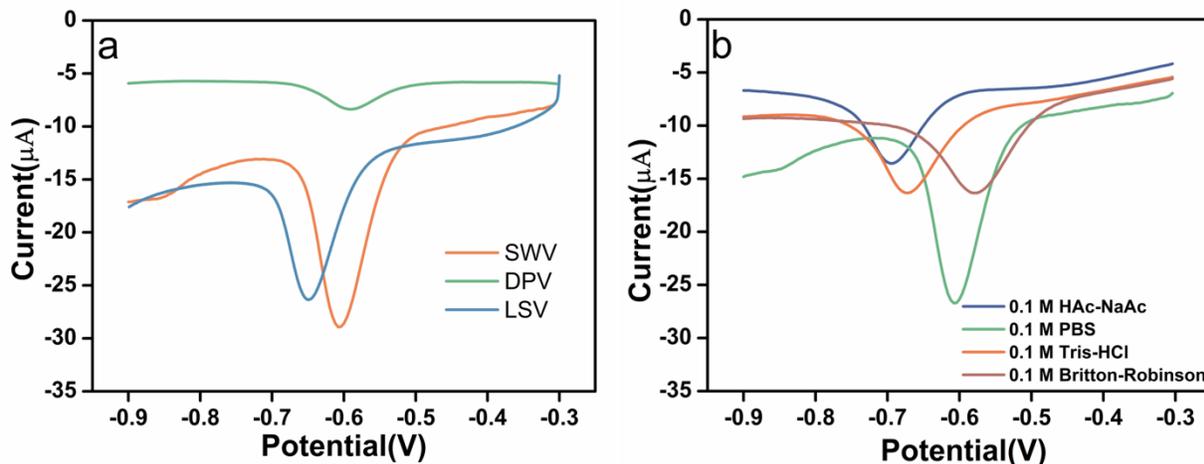


Fig. S2 (a) Current response of different methods in 0.1M PBS with 20µM AA (b) Current response of AA in different electrolytes

It can be clearly shown from Fig. S2(a) that the current intensity of AA detection via SWV method is the highest. Therefore, we choose SWV as the method for detecting. To investigate the strength of the electrochemical reaction of SWV of AA in different electrolyte solutions, four commonly used electrolyte solutions were selected and tested in their effective buffer range, namely, 0.1 mol/L Britton-Robinson buffer solution, 0.1 mol/L Tris-HCl buffer solution, 0.1 mol/L HAc-NaAc buffer solution, and 0.1 mol/L PBS buffer solution. It is obvious from Fig. S2(b) that the background currents in the solutions with different electrolytes differ very little but the current response of the AA varies greatly. However, the current response to AA varied greatly in size, and the current response in 0.1 mol/L PBS was the best, so PBS was chosen as the buffer solution for the experiment

References

1. Y. Wang, X. Mamat, Y. Li, X. Hu, P. Wang, Y. Dong and G. Hu, *Electroanalysis*, 2019, **31**, 1390-1400.