Electronic Supplementary Information for ***New Journal of Chemistry***

Self-assembly encapsulation of vanadium tetrasulfide into nitrogen doped biomass-derived porous carbon as a high performance electrochemical sensor for xanthine determination

Di Zhu [a,*], Jianjiao Xin [b], Xuemei Li [a,*]

[a] School of Chemistry and Chemical Engineering, Linyi University, Linyi, 276000, P.R. China

[b] College of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar, 161006, P.R. China

2.1 Materials and measurements

Xanthine (AR=Analytical reagent), sodium orthovanadate (AR), thioacetamide (AR), boric acid (AR), thioacetamide, urea, KOH *et al.* were purchased from Aladdin Biochemical Technology Co., Ltd. Other reagents were obtained from Guangfu company with analytic level.

The FT-IR absorption spectra were performed on the equipment type of Bruker Tensor II spectrometer ranging the wavenumber from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} with the KBr/sample mass ratio of 10/1. The XPS analysis was carried out using an equipment model of ESCALAB-MKII spectrometer with Al-Kα (1486.6 eV) as the X-ray source. Brurauer-Emmer-Teller surface area was calculated from nitrogen adsorption isotherms at 77 K using a V-Sorb 2800P instrument. Structure and morphology characteristics were examined by SEM (Hitachi S-4300, accelerating voltage as 5 kV, Japan), and TEM (JEM-2100, JEOL, Japan). The XRD pattern were done with the equipment of X′Pert-Pro MPD from Netherlands. The electrochemical characterizations were performed on the workstation CH Instruments 760E in 0.1 M PBS (pH = 6.0) at room temperature, and in the air. A platinum wire electrode and an Ag/AgCl electrode (with contained 3M KCl) were used as an auxiliary electrode and a reference electrode, respectively. The fabricated VS_4@N-BPC modified GCE was utilized as a working electrode. Differential pulse voltammetry (DPV) runs of the analyte were recorded in the potential range varying from −0.2 to +1.2 V, pulse amplitude 0.05 V, pulse period 0.5 s, and sampling width 0.0167 s. Cyclic voltammetry (CV) experiments were performed in the potential window of −0.2 to

+1.2 V at various scan rates (20 to 200 mV s^{-1}) in anodic stripping mode. Electrochemical impedance spectra (EIS) were recorded in 0.1 M PBS (pH = 7.0) containing 5 mM $[Fe(CN)_6]^{3-/4-}$ and 0.1 M KCl mixture solution in the frequency range of 0.005 Hz-100 kHz at an open circuit potential with a voltage amplitude of 5 mV.

2.2 Synthesis of VS_4 nanospheres

VS_4 was prepared as follows: Firstly, 3 mmol sodium orthovanadate (Na_3VO_4) was dissolved in 50 mL mixed solution (25 mL distilled water and 25 mL glycol contained 15 mmol thioacetamide). Secondly, the mixed solution was transferred into a 100 mL stainless steel reactor and maintained at 160 ℃ for 24 h. After several rounds of centrifugation and washing steps with distilled water and ethanol. The obtained VS_4 powder was vacuum dried at 80 ℃ for 12 h.

2.3 Synthesis of the Biomass-derived porous carbon

The natural birch bark was treated as the carbon source to synthesize the biomass-derived porous carbon. First, the birch bark was peeled out the exocuticle and dried absolutely at 60 ℃ for 12 h. Then, 8 g birch bark, 0.5 g urea and 0.1 M (100 mL) citric acid were mixed and transferred into an autoclave at 200 ℃ for 6 h. After that, the resulting products were gathered after filtration with water. The obtained product was grinded and soaked in 4 M KOH solution for 12 h, and then filtrated and washed with plentiful water until the filtrate was neutral. At last, the nitrogen doped

biomass-derived porous carbon (marked as N-BPC) was produced after drying at 80 ℃, and carbonization at 350 and 700 ℃ for 2 h under Ar atmosphere.

2.4 Real sample preparation

The use of human urine has been approved by all volunteers. In order to eliminate the interference factors and retain the complete tested component, before performing the real sample test, a series of pretreatments, including extraction, purification and dilution were carried out. In addition, the real sample test was repeated three times at least to reduce the experimental error.

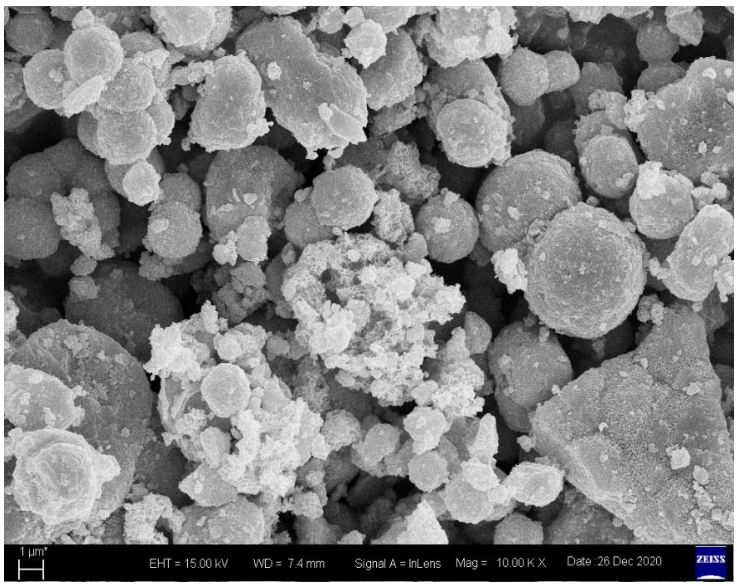

Fig. S1 The SEM image of VS_4 nanospheres.

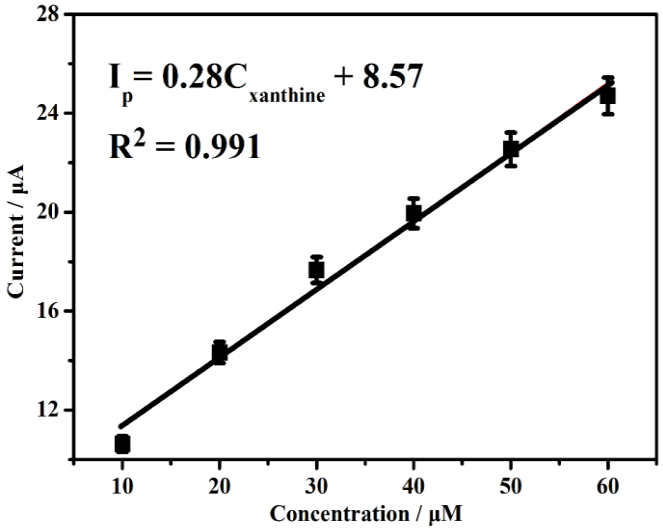

Fig. S2 The calibration curve of the proposed VS_4@N-BPC detection of xanthine.

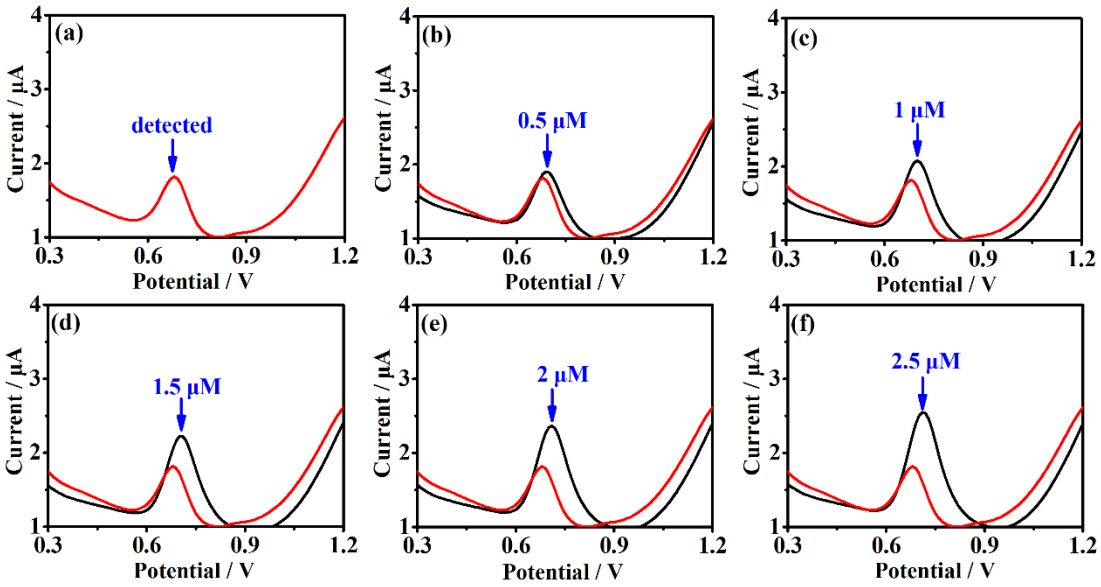

Fig. S3 DPV curves of the VS_4@N-BPC sensor in human urine with different concentrations of xanthine added; (a) the detected original concentration (red line); (b) 0.5 μM xanthine added (black line); (c) 1 μM xanthine added (black line); (d) 1.5 μM xanthine added (black line); (e) 2 μM xanthine added (black line); (f) 2.5 μM xanthine added (black line).