

Hierarchical sulfur doped scaly carbon coupled with cerium oxide nanoparticles based electrochemical sensor for the sensitive determination of uric acid

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2.1 Materials and measurements

Uric acid (AR=Analytical reagent), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (AR), sulfur powder (AR), citric acid (AR), poly dimethyl diallyl ammonium chloride, NaOH *et al.* were purchased from Aladdin Biochemical Technology Co., Ltd. Other reagents were obtained from Guangfu company with analytic level.

The XPS analysis was carried out using an equipment model of ESCALAB-MKII spectrometer with Al-K α (1486.6 eV) as the X-ray source. Structure and morphology characteristics were examined by SEM (Hitachi S-4300, accelerating voltage as 5 kV, 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 CeO₂@S-SC 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 CeO₂ nanoparticles

The CeO₂ was prepared as the following: In details, under 80°C, 25 ml of H₂O was heated for 20 min. Under magnetic stirring, Ce(NO₃)₃·6H₂O solution (0.5 g) was added followed by addition of NaOH (1 g). Then, the color of the solution became black within 30 s. After 10 minutes later, 1 ml of poly dimethyl diallyl ammonium chloride (PDDA) were further injected into the above mixture solution and kept at 120°C for 8 h. Finally, the CeO₂ nanoparticles was obtained after a series of washing, filtration and drying steps.

2.3 Synthesis of the CeO₂@S-SC materials

The natural seaweed was treated as the carbon source to synthesize the biomass-derived carbon. First, the seaweed was peeled out the exocuticle and dried absolutely at 60 °C for 12 h. Then, 8 g seaweed, 1 g CeO₂ powders, 0.5 g sulfur powders and 0.1 M (100 mL) citric acid were mixed and transferred into an autoclave at 200 °C 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 cerium oxide (CeO₂) nanoparticles anchored on sulfur-doped scaly carbon (marked as CeO₂@S-SC) was produced after drying at 60 °C, and carbonization at 350 and 700°C for 2 h under Ar atmosphere.

The synthesis process of sulfur-doped scaly carbon (S-SC) was similar to that for the preparation of CeO₂@S-SC, except there was no CeO₂ powders added.

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.

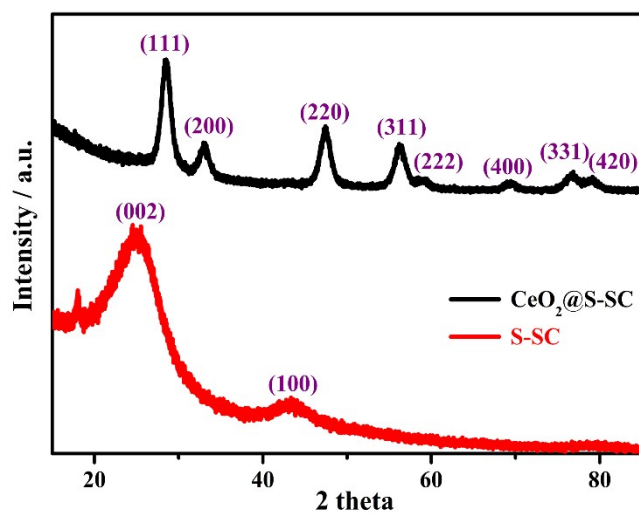


Fig. S1 XRD spectra of $\text{CeO}_2@\text{S-SC}$ and S-SC nanomaterial.

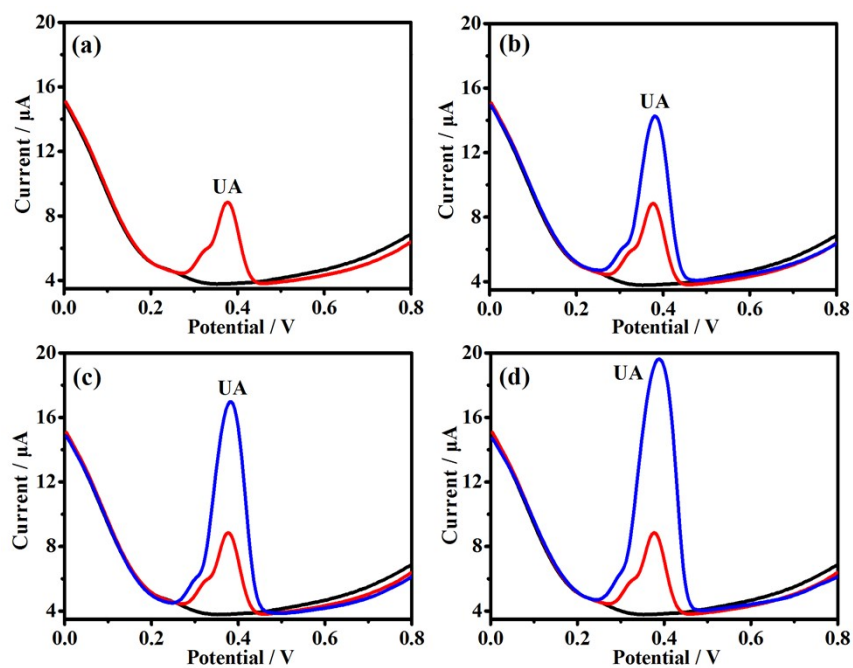


Fig. S2 DPV curves of the $\text{CeO}_2@\text{S-SC}$ sensor in human urine with different concentrations of UA; (a) the detected original UA concentration (red line); (b) 10 μM UA was added (blue line); (c) 20 μM UA was added (blue line); (d) 30 μM UA was added (blue line).

Table S1. Comparison of electrochemical impedance parameters.

Electrode	R_{ct} / Ω	R_s / Ω	CPE	W_o
Original SC	large	183.9	-	0.44
CeO ₂	552.2	178.7	0.87	0.48
CeO ₂ @S-SC	212.5	186.9	0.68	0.46