Supporting information

Electrochemical sensor based on $FeCo_2O_4$@ZIF-67/MWCNT-COOH for simultaneous detection of dihydroxybenzene isomers in different water systems

Hao Guo*, Wenting Niu, Zeyun Yang, Ruixue Yan, Jianpeng Ma, Yanyan Ma, Mingyue Wang and Wu Yang*

Key Laboratory of Eco-functional Polymer Materials of the Ministry of Education, Key Lab of Bioelectrochemistry and Environmental Analysis of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Gansu International Scientific and Technological Cooperation Base of Water-Retention Chemical Functional Materials, Lanzhou 730070, P R China.

S1 Materials and reagents

Urea was obtained from Sinopharm Group Chemical reagent Co., LTD. Carboxylated multiwalled carbon nanotubes (MWCNT-COOH) was the product of Shenzhen Suiheng Technology Co., LTD. 2-Methylimidazole was ordered from Shanghai Maclin Biochemical Technology Co., LTD. Iron(II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) was bought from Tianjin Kaixin Chemical Industry Co., LTD. Cobaltous nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and catechol (CC, AR) were the products of Xi 'an Chemical Reagent Factory. Hydroquinone (HQ, AR) and resorcinol (RC, AR) were produced by Tianjin Fengchuan Chemical Reagent Technology Co., Ltd. Absolute methanol and ethanol (99.7%) were provided by Li'an Long Bohua Pharmaceutical Chemical Co., LTD, Tianjin. N, N-Dimethylformamide (DMF) was obtained from Li 'an Long Bohua (Tianjin) Medicinal Chemical Co., Ltd. Phosphate buffer solution (PBS) was prepared by $Na_2HPO_4{\cdot}12H_2O$ and $NaH_2PO_4{\cdot}2H_2O$, which were obtained

Correspondence author.
Email: haoguo12@126.com (H. Guo), xbsfda123@126.com (W. Yang).

from Sinopharm Chemical Reagent Co., Ltd. All materials were of analytical grade and directly used without further purification. Redistilled water was used throughout the experiments.

S2 Apparatus and instruments

The morphology analysis of the modifiers was performed with scanning electron microscopy (SEM) (Zeiss Ultra Plus, Germany) and transmission electron microscopy (TEM) (FEI TecnaiG2-F20, USA). Fourier transform infrared spectra (FT-IR) of the samples were recorded on an FTS-3000 spectrometer (Digilab, USA). The powder X-ray diffraction (PXRD) patterns of materials were collected using the BRUKER X-ray diffractometer with Cu-Kα radiation (Germany). Brunauer-Emmett-Teller (BET) experiment was carried out in a liquid nitrogen atmosphere using a Micromeritics ASAP 2010 instrument (USA). Thermogravimetric analysis (TGA) was carried out using an SSC-5200 thermogravimetric analysis system (USA). The chemical states of the elements on the surface of the nanocomposite were measured by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, USA). All electrochemical tests including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and differential pulse voltammetry (DPV) were accomplished using a computer-controlled CHI 660E electrochemical workstation (Chen Hua Instruments Co., LTD, Shanghai, China), with a three-electrode system composed of a bare or modified glassy carbon electrode (GCE, diameter is 3 mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum sheet electrode as the counter electrode.

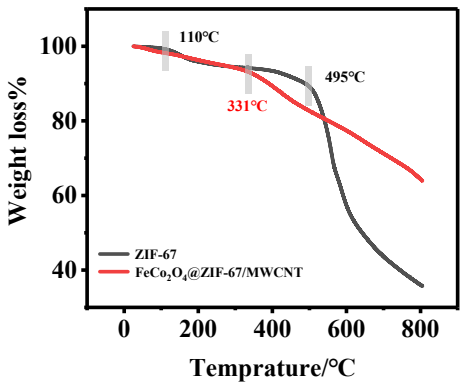

Fig.S1 Thermogravimetric analysis curves of ZIF-67 and $FeCo_2O_4$@ZIF-67/MWCNT-COOH.

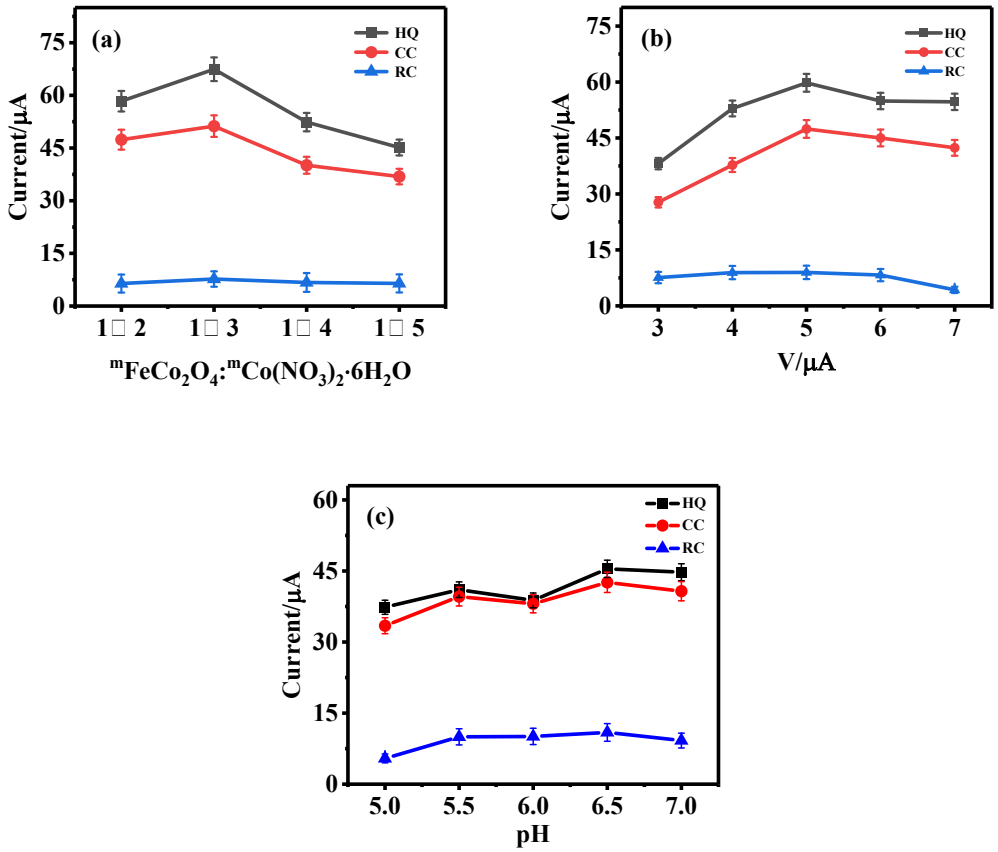

Fig.S2 Effects of **(a)** the mass ratio of $FeCo_2O_4$ to $Co(NO_3)_2·6H_2O$ during $FeCo_2O_4$@ZIF-67 synthesis, **(b)** coating amount of $FeCo_2O_4$@ZIF-67/MWCNT-COOH suspension and **(c)** pH of PBS on the oxidation peak currents.

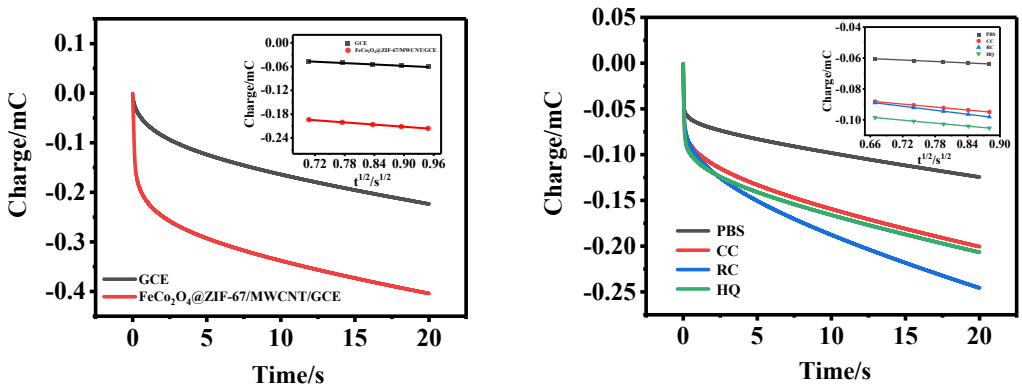

Fig.S3 (a) Chronocoulometric curves of bare GCE and $FeCo_2O_4$@ZIF-67/MWCNT-COOH/GCE in 0.1 mM $[Fe(CN)_6]^{3-/4-}$ containing 0.1 M KCl. **(b)** Chronocoulometric

curves of $FeCo_2O_4$@ZIF-67/MWCNT-COOH/GCE in the blank PBS and in PBS containing 200 μM CC, RC and HQ. The insets are corresponding plots of Q-$t^{1/2}$.