Supporting Information

3D C-Co-N-anchored MWCNTs derived from metal-organic frameworks as high-performance electrochemical sensing platforms for sensitive detection of Adrenaline

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Reagents and materials

Adrenaline Hydrochloride and 2-methylimidazole were provided by Aladdin Reagent Co., Ltd. (Shanghai, China); Anhydrous methanol, cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and anhydrous ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China); multi-walled carbon nanotubes (MWCNTs) was supplied from Xianfeng Nano Technology Co., Ltd. Other chemicals and reagents are all of the analytical grade and without any further purification. For human serum samples, we obtained blood samples from local hospitals, centrifuged and collected serum samples, then added a certain concentration of adrenaline standard solution to the serum samples. 0.1 $mol \cdot L^{-1}$ phosphate buffer solution was prepared by mixing 0.1 $mol \cdot L^{-1}$ NaH_2PO_4/Na_2HPO_4 with 0.1 $mol \cdot L^{-1}$ KCl. The experimental water is double deionized water.

Characterization

X-ray diffraction (XRD, Bruker D8 Advance) was used to determine the crystal phase. Scanning electron microscopy (SEM, Hitachi S4800) and transmission electron microscopy (TEM, FEI, Talos F200X) were applied to examine the morphologies. An N_2 adsorption-desorption isotherm was used to study the specific surface area and pore size distribution of produces (Beishide, 3H-2000PS4). The Thermo Scientific K-Alpha was used to measure X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, ESCALABMK II).

Electrochemical experiments were performed on a CHI660D electrochemical workstation (Shanghai Chenhua Co., China). During Ad detection, the measurements were detected using a traditional three-electrode setup consisting of a platinum wire as the counter electrode, a glass carbon electrode (GCE, = 3 mm) as the working electrode, and Ag/AgCl (saturated KCl saturated solution) as the reference electrode. Cyclic voltammetry (CV) was performed at a scan rate of 100 mV/s from -0.2 V to 0.6 V, and differential pulse voltammetry (DPV) was performed at a pulse amplitude of 0.05 V from -0.2 V to 0.6 V. At the open circuit voltage, electrochemical impedance spectroscopy (EIS) was performed with a frequency swept from 0.1 to 10 KHz and an amplitude of 5 mV.

Pretreatment of MWCNTs

Before the use of MWCNTs, the purchased MWCNTs were processed to functionalize their surface with active groups. 5.0 g MWCNTs and 150 mL concentrated nitric acid was typically combined in a round-bottomed flask and ultrasonically processed for 1 hour. After that, the mixture was heated to 120°C and held in an oil bath for 24 hours with constant stirring. The pretreated-MWCNT precipitates were rinsed with deionized water multiple times to obtain neutral pH and dried in vacuum after filtering the suspension.

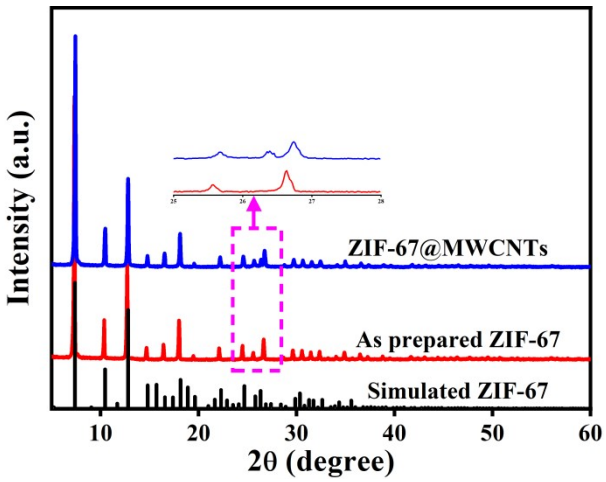

Fig. S1 XRD spectras of ZIF-67 and ZIF-67@MWCNTs.

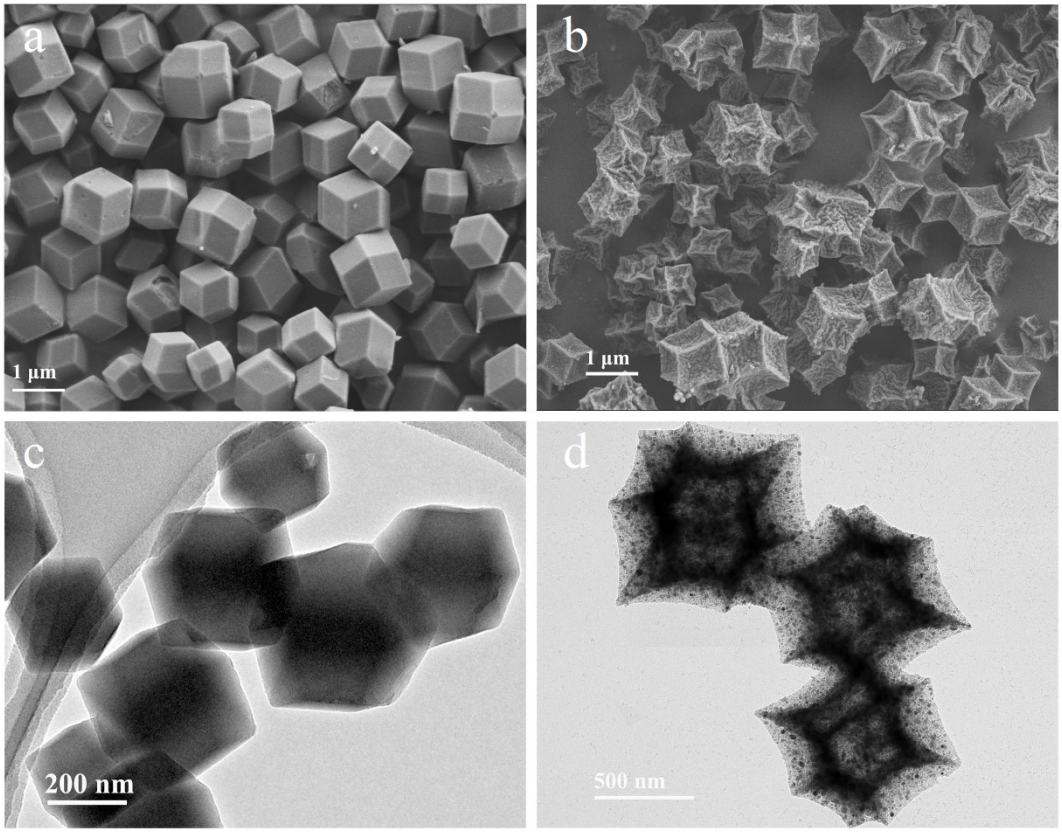

Fig S2 (a) SEM and (c) TEM of images of ZIF-67; (b) SEM and (d) TEM of images of C-Co-N.

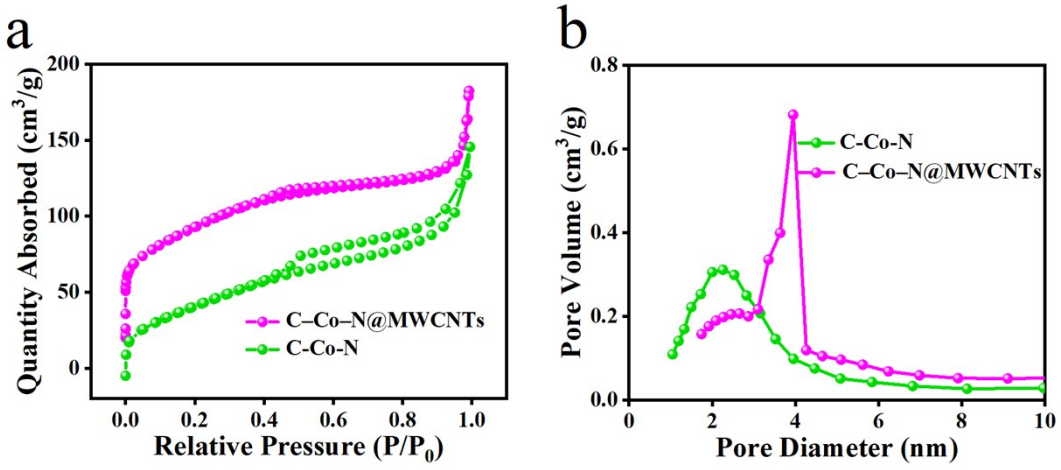

Fig. S3 (a) Nitrogen adsorption-desorption isotherms and (b) Pore-size distribution of C-Co-N and C-Co-N@MWCNTs.

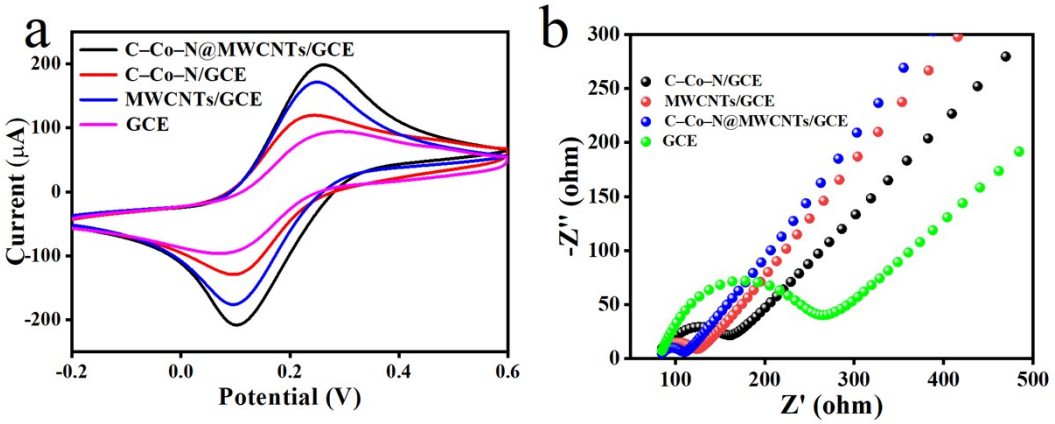

Fig. S4 CV at scan rate of 100 $mV \cdot s^{-1}$ (a) and EIS of different electrodes in 0.1 $mol \cdot L^{-1}$ KCl solution containing 5 $mmol \cdot L^{-1}$ $[Fe(CN)_6]^{3-/4-}$.

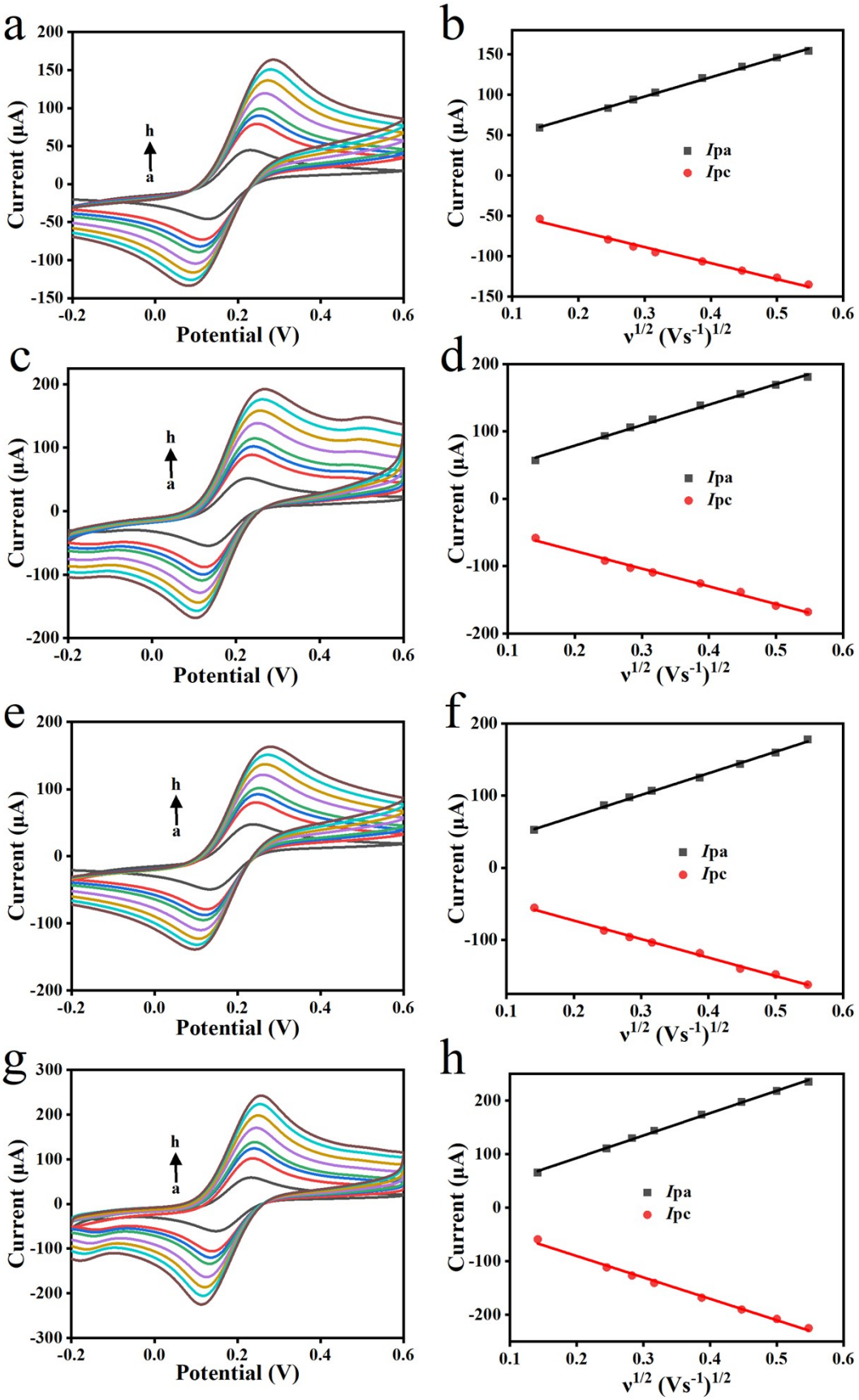

Fig. S5 CV of GCE (a, b), C-Co-N/GCE (c, d), and C-Co-N@MWCNTs/GCE (e, f) in 5 mmol· L^{-1} $K_3[Fe(CN)_6]$ solution (containing 0.1 mol·L^{-1} KCl) at different scan rates (a to h: 20,

60, 80, 100, 150, 200, 250, 300 mV·s^{-1}).

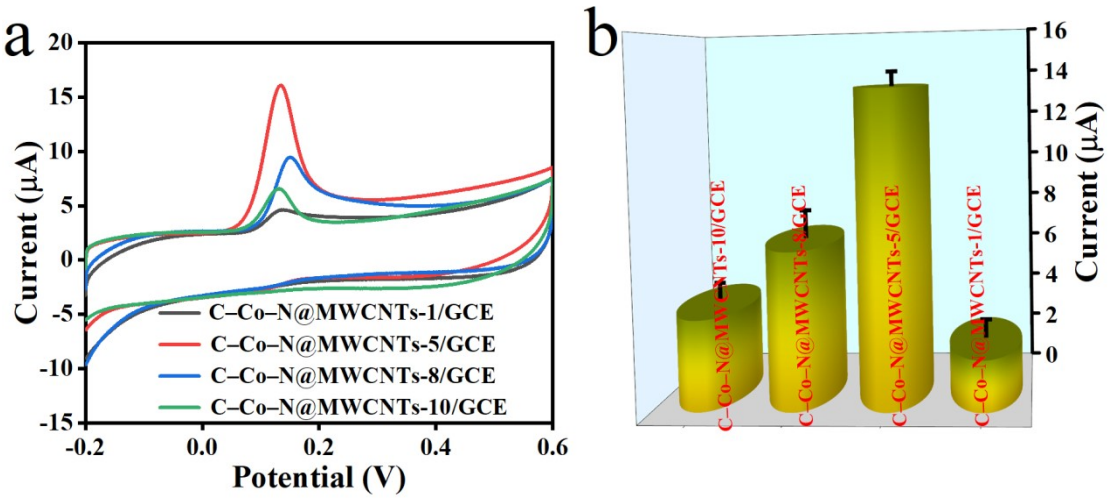

Fig. S6 CVs response of Ad (0.1 mmol·L^{-1}) at C-Co-N@MWCNTs-1/GCE, C-Co-N@MWCNTs-5/GCE, C-Co-N@MWCNTs-8/GCE, and C-Co-N@MWCNTs-10/GCE in PBS (pH 7.0).