Supporting Information

A 3D-Graphene Fiber Electrode Embedded with Nitrogen-Rich-Carbon-Coated ZIF-67 for the Ultrasensitive Detection of Adrenaline

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Experimental Section

1. Materials

All chemicals and reagents were of analytical grade and used as received without further purification. Hydrochloric acid, sulfuric acid, potassium dihydrogen phosphate (KH_2PO_4) and disodium hydrogen phosphate (Na_2HPO_4) were purchased from Beijing Chemical Works (China). Potassium chloride, cobalt nitrate hexahydrate ($Co(NO_3)_2•6H_2O$), 2-methylimidazole, ascorbic acid (AA), uric acid (UA), tyrosine (Tyr) and alanine (Ala) and acetaminophen (AC) were obtained from Aladdin. Adrenaline (Ad) was purchased from Sigma. Potassium perchlorate ($LiClO_4$) was purchased from Tianjin Guangfu Fine Chemical Research Institute (China). Potassium ferricyanide ($K_3Fe[(CN)_6]$) was obtained from Tianjin Jinke Fine Chemical Research Institute (China). Ethanol and methanol was acquired from Beijing Tong Guang fine chemical Co., Ltd. All solutions were prepared with ultrapure water produced by a Milli-Q system (18.2 MΩ, Millipore, USA).

2. Experimental Section

2.1 Preparation of 0.1 M phosphate buffer (PBS, pH 7.0)

In a typical synthesis, 2.26816 g of KH_2PO_4 was added to a beaker (250 mL), followed by 11.9380 g of Na_2HPO_4. The mixture was dissolved in about 200 mL of ultrapure water. Finally, the mixed solution was transferred to a volumetric flask (500 mL), diluted with ultrapure water to volume and mixed. The obtained PBS was stored at room temperature.

2.2 Preparation of 5 mM potassium ferricyanide solution ($K_3Fe[(CN)_6]$)

Typically, 1.86375 g of KCl powder (0.1 M) and 0.411560 g of $K_3Fe[(CN)_6$ were dissolved in ultrapure water. The mixed solution was transferred to a 250 mL volumetric flask, diluted with ultrapure water to volume, and mixed. The obtained 5 mM $K_3Fe[(CN)_6$ was stored at 4 °C.

2.3 Fabrication of ZIF-67/NC/3DG fiber

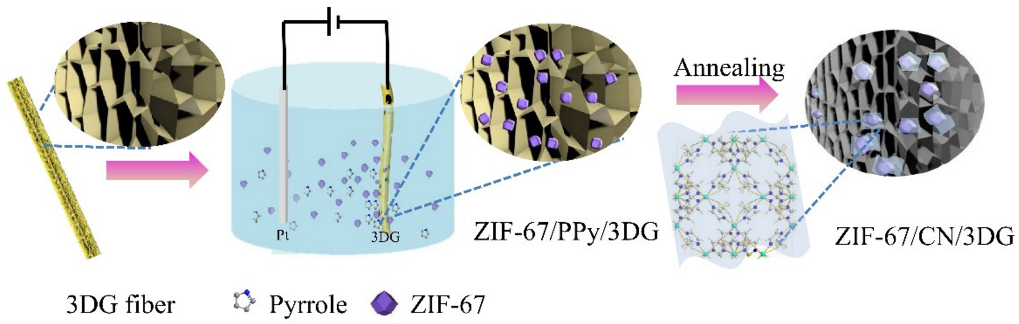

Fig. S1 Schematic of the fabrication process of ZIF-67/NC/3DG fiber.

Synthesis of 3DG fiber: Graphene oxide (GO) was firstly synthesized by oxidation of graphite powder according to the modified Hummers method.[1] Then three-dimensional graphene oxide (3DGO) fiber was prepared similar to a wet spinning strategy.[2] Typically, 5 mL GO (20 mg/mL) was spun into liquid nitrogen with a speed of 0.5 m/s by an injector (with a diameter of 0.25 mm), followed by freeze-drying. To obtain 3DG fiber, the 3DGO fiber was heated to 200 ^{o}C for 2 h at first and then further heated to 1000 ^{o}C for 2 h with a heating speed of 10 ^{o}C/min under N_2/H_2 (V:V=4:1) atmosphere.

Synthesis of ZIF-67: ZIF-67 was synthesized according to the literature.[3] Typically, cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 3.492g) was dissolved in a mixed solution (60 ml) of ethanol and methanol (V:V =1:1). Then 2-methylimidazole (3.94 g) was added to the 60 ml mixed solution of ethanol and methanol (V:V=1:1) and stirred. The mixture was kept for 20 h at room temperature under continuous stirring. The purple precipitate was centrifuged, washed several times with methanol and dried at 80 ^{o}C.

Synthesis of ZIF-67/NC/3DG fiber: The ZIF-67 particles (1.20 mg) were dispersed in a mixed solution of 15 μL of pyrrole monomer, 0.1064 g of lithium perchlorate ($LiClO_4$) and 10 ml of phosphate buffer (PBS). The mixture was keep stirring during the process of electrochemical deposition to form ZIF-67/PPy/3DG. The as-synthesized bare 3DG fiber with 2.0 mm in length was used as the working electrode, a commercial Pt plate was used as counter electrode and a saturated calomel electrode (SCE) as reference. The ZIF-67/PPy/3DG was fabricated by a cyclic voltammetry electrodeposition method of ZIF-67 and pyrrole on the 3DG fiber surface in the potential range from -0.1 to 0.75 V vs. SCE, sweep segments were set at 10. The ZIF-67/PPy/3DG fiber was annealed at 350 ^{o}C in air for 2 h with a ramp rate of 10 ^{o}C/min, the obtained product was denoted as ZIF-67/NC/3DG.

3. Characterization and measurements

The morphology of the fiber electrodes were measured using a scanning electron microscope (SEM, ZEISS). X-Ray Diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray powder diffractometer. X-ray photoelectron spectroscopy (XPS) data was carried out using an ESCALab220i–XL electron spectrometer from VG Scientific using 300 W Al-Kα radiation. The electrochemical sensing properties of fiber electrodes toward Ad were studied in a 0.1 M phosphate buffer (PBS, pH=7.0) at room temperature, using an electrochemical workstation (CHI 760E, China) with a three-electrode system. All of the solutions were deoxygenated by bubbling high purity N_2 (99.999%) for 30 min before electrochemical measurements, if not specifically mentioned.

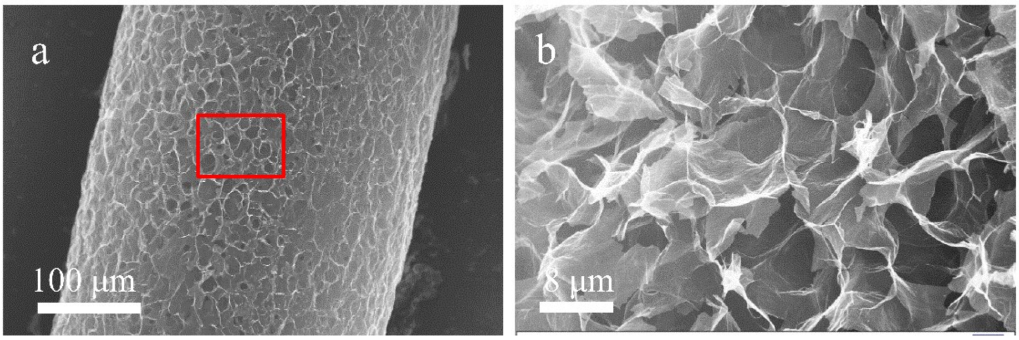

Fig. S2 (a) Scanning electron microscopy (SEM) image of bare 3DG. (b) The enlarged view of the rectangle area in (a).

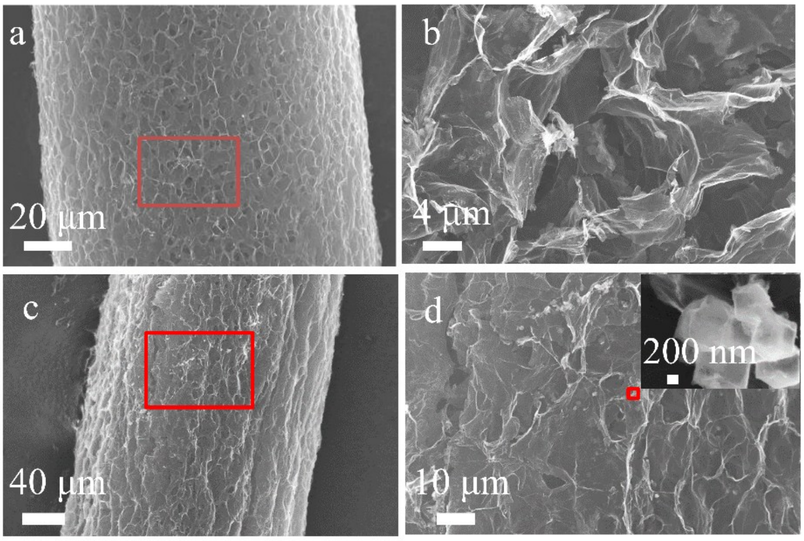

Fig. S3 (a) SEM image of NC/3DG fiber. (b) The enlarged view of the rectangle area in (a). (c) SEM image of ZIF-67/3DG fiber. (d) The enlarged view of the rectangle area in (c). The inset in (d) is an enlarged SEM image of the ZIF-67.

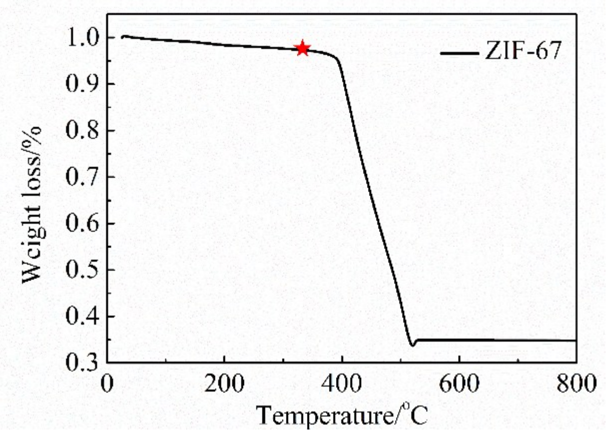

Fig. S4 Thermogravimetric analysis (TGA) curves of ZIF-67, the red star mark corresponding to 350 °C.

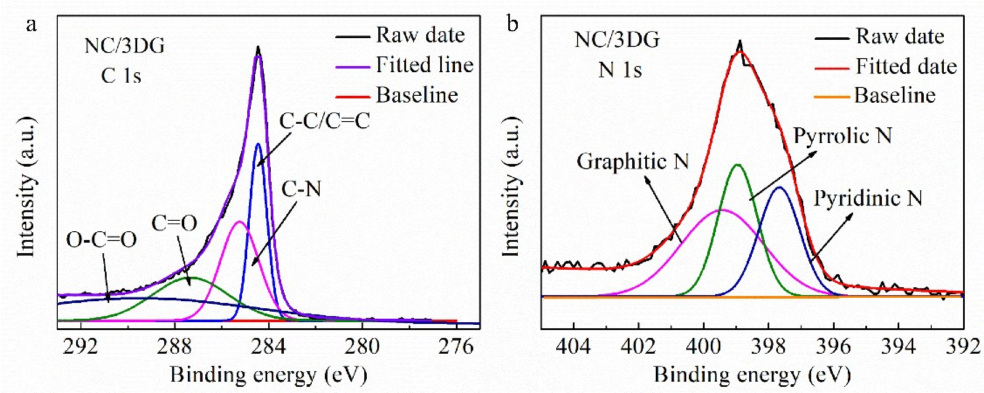

Fig. S5 (a, b) The high-resolution C 1s and N 1s peak of NC/3DG.

For comparison, a series of ZIF-67/NC/3DG samples with different contents of polypyrrole were obtained by adjusting the sweep segments (y=0, 20 and 30) while keeping the content of ZIF-67 constant, which were designed as ZIF-67_m/NC/3DG, ZIF-67_m/NC_{20}/3DG and ZIF-67_m/NC_{30}/3DG, respectively. In addition, a series of ZIF-67_m/NC_{10}/3DG samples with different contents of ZIF-67 were prepared by adjusting the added quantity (m=0.6, 3m=2.02 mg) in the same process, which were named as ZIF-67_m/NC_{10}/3DG and ZIF-67_{3m}/NC_{10}/3DG.

Table S1. The elemental content (at %) of ZIF-67_m/NC_{10}/3DG, ZIF-67_{2m}/NC_{10}/3DG and ZIF-67_{3m}/NC_{10}/3DG determined by EDX.

Sample	C	N	O	Co
ZIF-67_m/NC_{10}/3DG	85.17	5.240	9.460	0.1300
ZIF-67_{2m}/NC_{10}/3DG	81.61	4.570	13.460	0.3600
ZIF-67_{3m}/NC_{10}/3DG	90.33	1.940	7.180	0.5500

The cyclic voltammograms (CVs) were obtained in the potential range from -0.4 to 0.6 V vs. SCE in a 0.1 M phosphate buffer (PBS, pH=7.0) at different scan rates (Fig. S6). The high concentration of Ad (9.5 μM) was chosen to provide a high concentration of depolarizer in the diffusion layer at the surface of fiber electrode.[4] The oxidation and reductive peak current value increased with increasing scan rate and the oxidation peak current value (I) was directly proportional to the square root of the scan rate (v), indicating the redox reaction of Ad at the fiber electrode is a typical diffusion controlled process.[5] In addition, two reduction peaks were observed, confirming the Ad electrochemical oxidation on the ZIF-67/NC/3DG fiber electrode is an irreversible process.

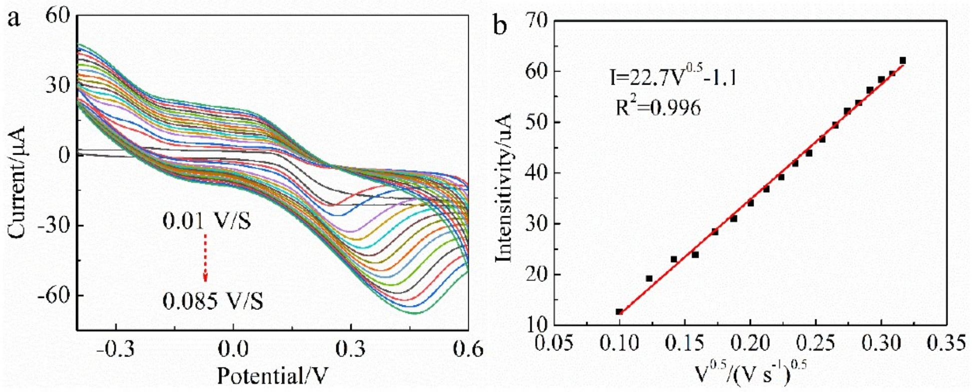

Fig. S6. (a) CVs obtained at the ZIF-67/NC/3DG fiber electrode in the potential range from -0.4 to 0.6 V vs. SCE at various scan rates from 0.01 V/s (inner) to 0.085 V/s (outer), 9.5 μM Ad. (b) Plot of the oxidation peak current versus the square root of the scan rate.

Table S2 Comparison of previously reported adrenaline sensors based on metal or carbon based electrodes

Electrode	Technique	Linear range (μM)	LOD (μM)	Ref.
Au nanotube array electrode	DPV	10–150	2.8	30
Au-Pd/rGO	DPV	0.001–1000	0.0012	31
ZNFe$_2$O$_4$/CPE	DPV	6.5–145	3	32
CuFe$_2$O$_4$/ILs/CPE	SWV	0.1–400	0.07	33
DWO/SPE	DPV	1–900	0.5	34
SiO$_2$-modified CPE	CV	1–60	0.6	35
BDDFE	SWV	0.7–60	0.21	36
DOPA-MWCNT-GCE	DPV	2.0–13.2	0.62	37
MXene/GCPE	CV	0.02–10 10–100	0.009	38
CPE-GO-EDDPT	DPV	1.5–600	0.65	39
ZIF-67/NC/3DG	DPV	0.06–95 95–5900	0.02	This work

Ascorbic acid (AA), uric acid (UA), tyrosine (Tyr) and alanine (Ala) coexist with Ad in the human body, and acetaminophen (AC) is often used to treat pain in the human body. So, from a clinical point of view, the determination of Ad with higher concentrations of interfering compounds is very important. Under the same conditions as the previous tests, in the mixed solution, the concentrations of interfering compounds were changed while keeping the concentration of Ad constant. Fig. 3e shows that the oxidation peak current of AA, UA, AC, Tyr and Ala increase with the increasing concentration from 95 to 640 μM. The corresponding AA and AC linear functions are I_{AA} =0.0044C_{AA}+0.174 and I_{AC} =0.0019C_{AA}-0.080 with a correlation coefficient of R^2=0.992 and 0.990, respectively (Fig. S7). In the above cases, Ad concentration was maintained at 95 μM, demonstrating that the ZIF-67/NC/3DG fiber electrode is more selective toward interfering compounds (AA, UA, AC, Tyr and Ala) even in the presence of high concentrations of interfering compounds.

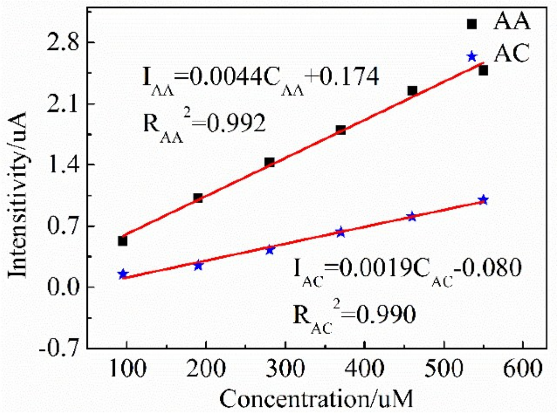

Fig. S7. Plots of oxidation peak current versus AA and AC concentration range from 95 to 640 μM.

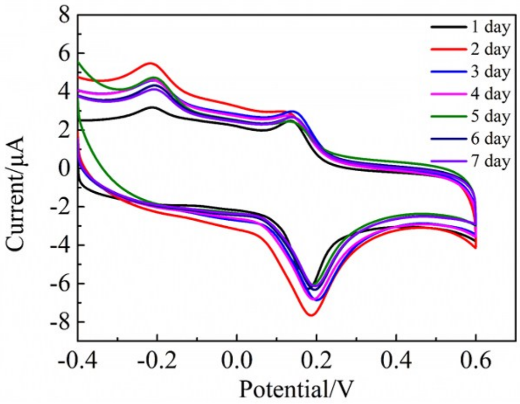

Fig. S8. CVs of ZIF-67_{2m}/NC_{10}/3DG in a solution containing 95 μM Ad.

Considering that the content of ZIF-67 and NC as well as annealing temperature have significant effects on the performance of the microelectrode, various ZIF-67_{2m}/NC_y/3DG (y=0, 5, 10, 20 and 30), ZIF-67_m/NC_{10}/3DG (m=0.6 1.20 and 2.02 mg) and ZIF-67_{2m}/PPy_{10}/3DG microelectrodes were obtained by the electrochemical deposition method. The electrochemical performance of all the above microelectrodes were evaluated in $K_3Fe(CN)_6$ solution by the cyclic voltammetry (CV) method (Fig.

S9-S11).

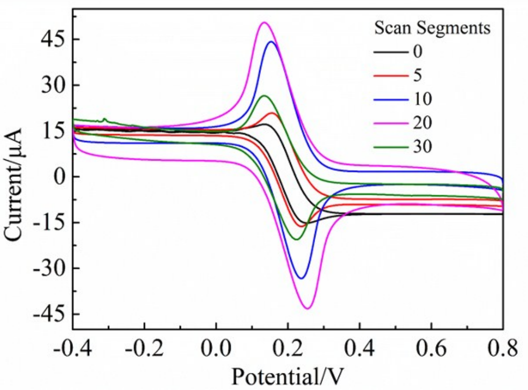

Fig. S9. Cyclic voltammograms (CVs) of ZIF-67_{2m}/$3DG_{350}$, ZIF-67_{2m}/NC_5/$3DG_{350}$, ZIF-67_{2m}/NC_{10}/$3DG_{350}$, ZIF-67_{2m}/NC_{20}/$3DG_{350}$, ZIF-67_{2m}/NC_{30}/$3DG_{350}$ in a solution containing 5 mM $[Fe(CN)_6]^{3-/4-}$.

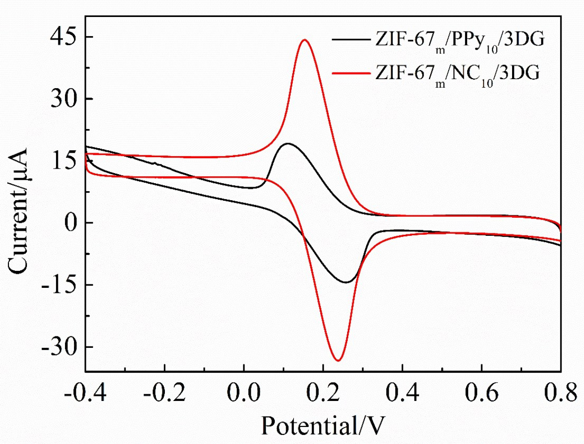

Fig. S10. CVs of ZIF-67_{2m}/PPy_{10}/3DG and ZIF-67_{2m}/NC_{10}/3DG in a solution containing 5 mM $[Fe(CN)_6]^{3-/4-}$.

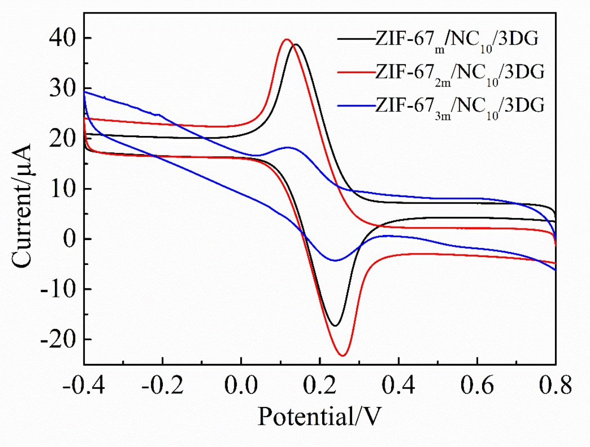

Fig. S11. CVs of ZIF-67_{m}/NC_{10}/3DG, ZIF-67_{2m}/NC_{10}/3DG and ZIF-67_{3m}/NC_{10}/3DG in a solution containing 5 mM $[Fe(CN)_6]^{3-/4-}$.

References

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