Electronic Supplementary Information
For

Linear Graphene Edge Nanoelectrode

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EXPERIMENTAL METHODS

Materials and Chemicals. CVD graphenes were grown on Cu foil. Potassium ferricyanide, potassium chloride, ferric chloride, ethyl alcohol were purchased from Sinopharm Chemical Reagent Co, Ltd.. Poly(methyl methacrylate) (PMMA, # P107082) was purchased from Aladdin Industrial Corporation. Aluminum oxide, UA, AA, EP were purchased from Sigma-Aldrich Co. LLC. All chemicals were of analytical-reagent grade. Deionized water (Milli-Q water purification system; Millipore, USA) was used through all the experimental procedures. All experiments were carried out at room temperature.

Apparatus. All electrochemical measurements were performed on an EC epsilon potentiostat/galvanostat connected to a BASi C3 Cell Stand (Bioanalytical Systems, Inc.) with a conventional three-electrode cell. The working electrode was a graphene nanoelectrode, or a carbon fiber microelectrode (CFME), or a glass carbon electrode (GCE, Φ = 3.0 mm) an Ag/AgCl electrode was used as reference electrode, the auxiliary electrode consisted of a platinum wire. Raman spectra were recorded on a Raman microscope (LabRam HR Evolution) with a 514.5 nm laser. High resolution transmission electron microscope (HR-TEM) images were taken with a JEOL 2010 microscope.

Preparation of electrode. The procedure for constructing graphene nanoelectrodes is illustrated in Fig.S1[1, 2]. 5% PMMA solution was coated on the graphene/copper foil and dried at 170 °C for 5 min. Because graphene grew on both sides of the Cu foil, the opposite side was polished to remove the graphene layer. The PMMA/graphene/copper sheet was immersed in $FeCl_3$ solution (1M $FeCl_3$+0.1 M HCl) to etch away the copper substrate and the PMMA/graphene film was floated on the surface of the solution. The floating graphene film was transferred with a watch glass to ultrapure water to remove the excess of the $FeCl_3$. Then the film was washed with 10% HCl solution three times to remove the residual metal ion, rinsed with water for several times and dried in air. The side with graphene was connected with copper wire using conductive resin adhesive. The entire assembly was subsequently placed in a mold filled with epoxy resin, which was allowed to solidify at room temperature for 24 h. Subsequently, the nanoelectrode was removed from the mold and graphene edge was exposed by cutting away the epoxy resin at end with a blade. The graphene nanoelectrode was ready for use after washing with water finally.

For comparison purposes, a GCE was polished with 10 μm Al_2O_3 slurry, subsequently rinsed with water and sonicated in distilled water and ethanol; a 7 μm diameter carbon fiber disk microelectrode (CFME) was activated by electrochemical method, first with constant-potential amperometry at 2.0 V for 60 s, at -1.0 V for 30 s, and then with cyclic voltammetry in 0.5 M H_2SO_4 within a potential range from 0 to 1.0 V at 10 mV/s until a stable cyclic voltammogram was obtained[3]. The detailed preparation of CFME can be found in the literature [4].

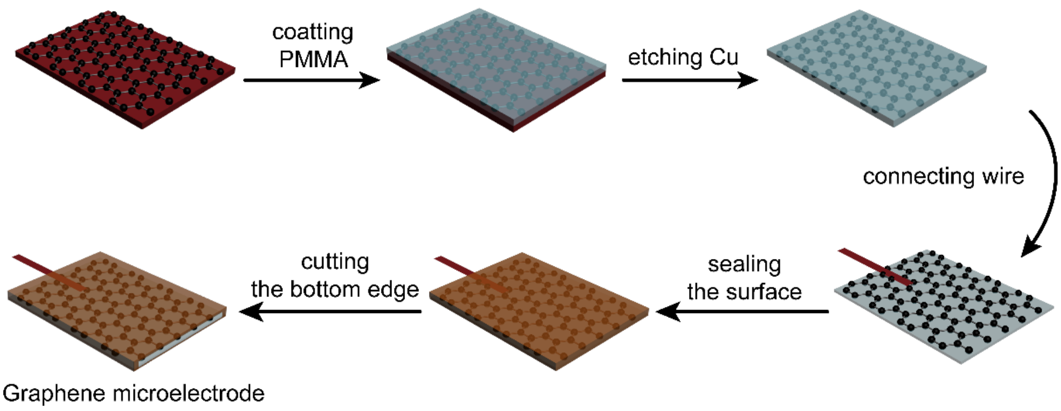

Fig.S1 The procedure for constructing graphene nanoelectrodes.

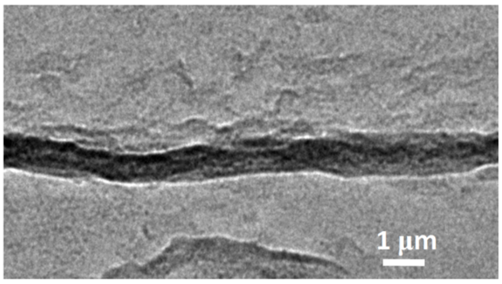

Fig. S2 A low magnification cross-section TEM image of a fabricated GNE sealed within epoxy resin, showing no apertures and cracks within the compact edge.

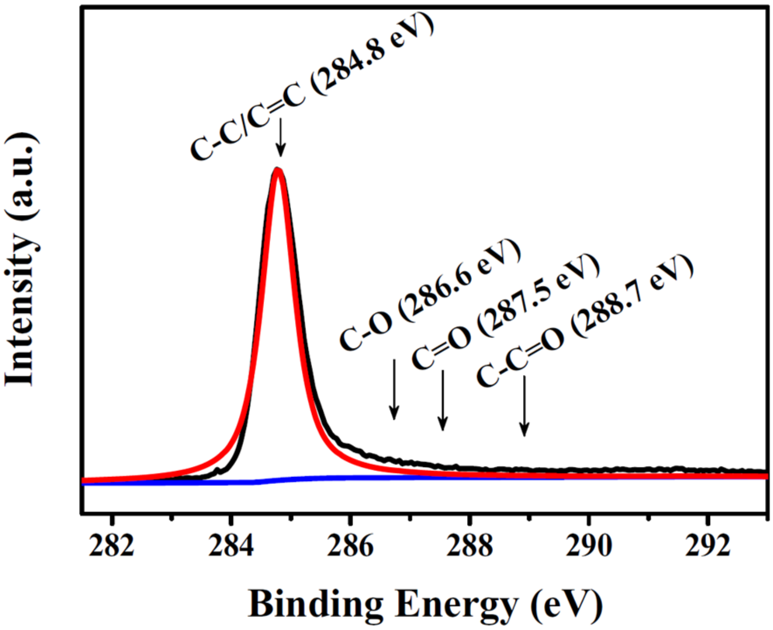

Fig. S3 High resolution XPS spectra of C1s peak of the graphene film, which reflects the presence of C=C/C–C bonds (～284.8 eV) but absence of C–O (hydroxyl and epoxy, ～286.6 eV), C=O (carbonyl, ～287.5 eV) and O–C=O (carboxyl, ～288.7 eV) bonds.

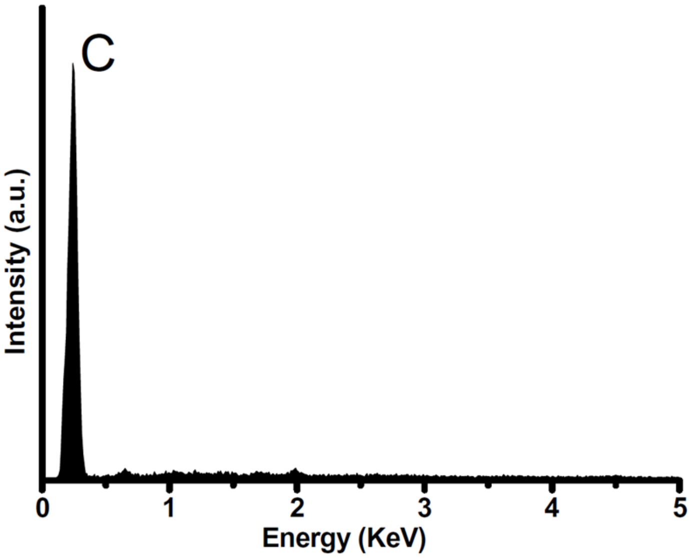

Fig. S4. Energy-dispersive spectroscopy (EDS) of graphene film, revealing the sample mainly consists of carbon.

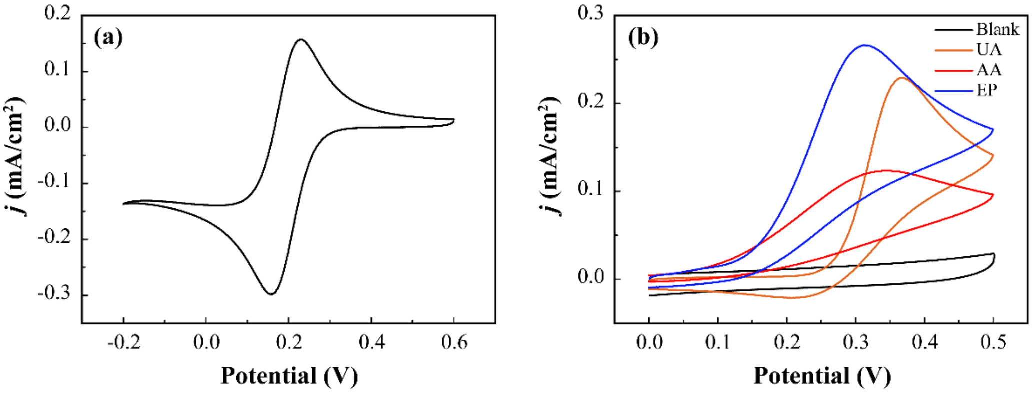

Fig.S5 (a) Cyclic voltammograms of 5 mM $K_3Fe(CN)_6$ in 0.1 M KCl on GCE at the scan rate of 5 mV/s; (b) Cyclic voltammograms of 1 mM UA (orange), 1 mM AA (red) and 1 mM EP (blue) in 0.1 M PBS (pH 7.0) on GCE at the scan rate of 50 mV/s.

References

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