A Facile Synthesis of Perforated Reduced Graphene Oxide for High Performance Electrochemical Sensor

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Experimental

Chemicals and solutions

Standard stock solution of selenium was purchased from Acros Organics. Graphene oxide was obtained from Nanjing XFNANO Materials Tech Co., Ltd. (Nanjing, China).Chlorauric acid ($HAuCl_4$), potassium hexacyanoferrate(II)trihydrate ($K_4Fe(CN)_6$), potassium ferricyanide(III) ($K_3Fe(CN)_6$), ferrous sulfate ($FeSO_4$), potassium chloride (KCl) was supplied by Sinopharm Chemical Reagent (Shanghai, China). All other chemicals were analytical reagents that have not been further purified. Deionized water (18.2 MΩ cm specific resistance), obtained from Pall Cascada laboratory water system, was used throughout the experience.

Apparatus.

Electrochemical experiments, including cyclic voltammetry (CV), linear sweep voltammetry (LSV) and square wave voltammetry (SWV) were performed on a CHI 660E electrochemical workstation (ChenHua, Shanghai, China). The modified GCE (3 mm in diameter) was used as the working electrode, with an Ag/AgCl electrode and platinum foil serving as the reference and counter electrodes, respectively. All potential values given below refer to Ag/AgCl. The synthetic nanocomposites were characterized by using scanning electron microscopy (SEM Hitachi S-4800 microscope, Japan), energy dispersive X-ray spectroscopy (EDX HORIBAEX-350 Japan).

Preparation of P-rGO and P-rGO/AuNDs modified electrode

Prior to modification, the GC electrode was thoroughly polished with 0.3 μm and 0.05 μm aqueous slurries of alumina powder, and then sonicated for 3 min in ethanol and water respectively. Perforated-shaped 3D-rGO were synthesized via one-pot electrochemical deposition and then self-sacrificed Prussian Blue. Firstly, the GC electrode was immersed in 30 mM $K_3Fe(CN)_6$ + 30 mM $FeSO_4$ + 0.5 mg/mL rGO aqueous solution to electrochemically electrodeposit rGO@PB films with cyclic vpltammetry at the potential range of -1.6 and 1.0 V with the scan rate of 0.2 V s^{-1}. V

for 50 cycles. Then rGO@PB modified electrode was rinsed with ultrapure water thoroughly. Then the electrode treated by the moderate of 0.5 M NaOH and 0.1 M H_2SO_4 soultion for five minutes to remove the PB analogues. The electrode was immersed in 1.0 mM chlorauric acid containing 0.2 M sodium sulfate solution to electrochemically electrodeposit Au nanodendrites with constant potential at -0.2 V for 20 s, and prepared the AuNDs/P-rGO electrode. Then the obtained GC/AuNDs/P-rGO was washed carefully with deionized water and then dried at room temperature. For comparison, rGO, P-rGO or AuNDs/rGO coated GCE was prepared with the same process, respectively.

Electrochemical analysis procedure

Unless stated otherwise, the experiments were carried out in the 0.1 M phosphate buffer saline (pH 7.0). linear sweep voltammetry (LSV) scans over the potential range from -0.2 V to 0.8 V with scan rate of 0.1 V/s and an equilibrium time was 2 s. Square wave voltammetry (SWV) scans over the potential range from 0 V to 0.6 V were recorded by using the following parameters: amplitude of 0.025 V and an equilibrium time of 2 s.

Results and discussion

Characterization of P-rGO modified electrode

The compositions of the as-prepared composites were carried out by EDS analysis. The bare glass electrode, planar contour of rGO@PB and crumped structure of P-rGO can be observed from Fig. S1. As shown in Fig. S1a and S1c, only the elements of C, O were detected, but the intensity of the element C in Fig. S1c is greater than the intensity of C in Fig. S1a. And from the Fig. S1b, the elements of C, O, Fe, S, K were were the major elements in rGO/@PB composites. C came from rGO, while Fe, S and K were from PB.

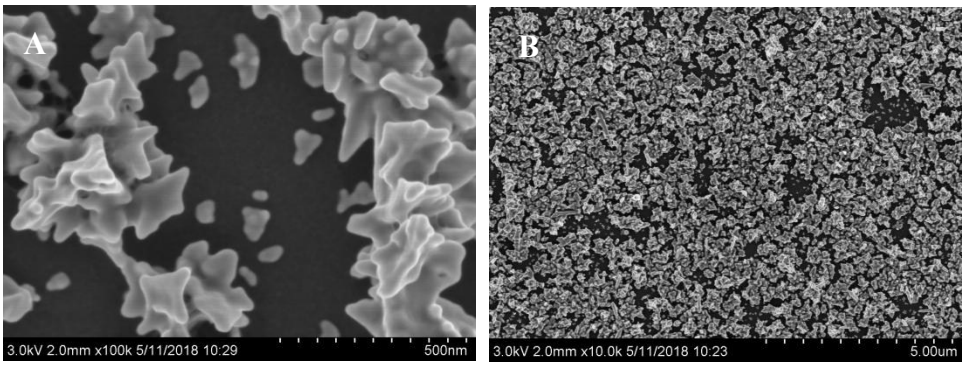

Fig. S1 SEM image of GC/P-rGO/AuNDs (A, B)

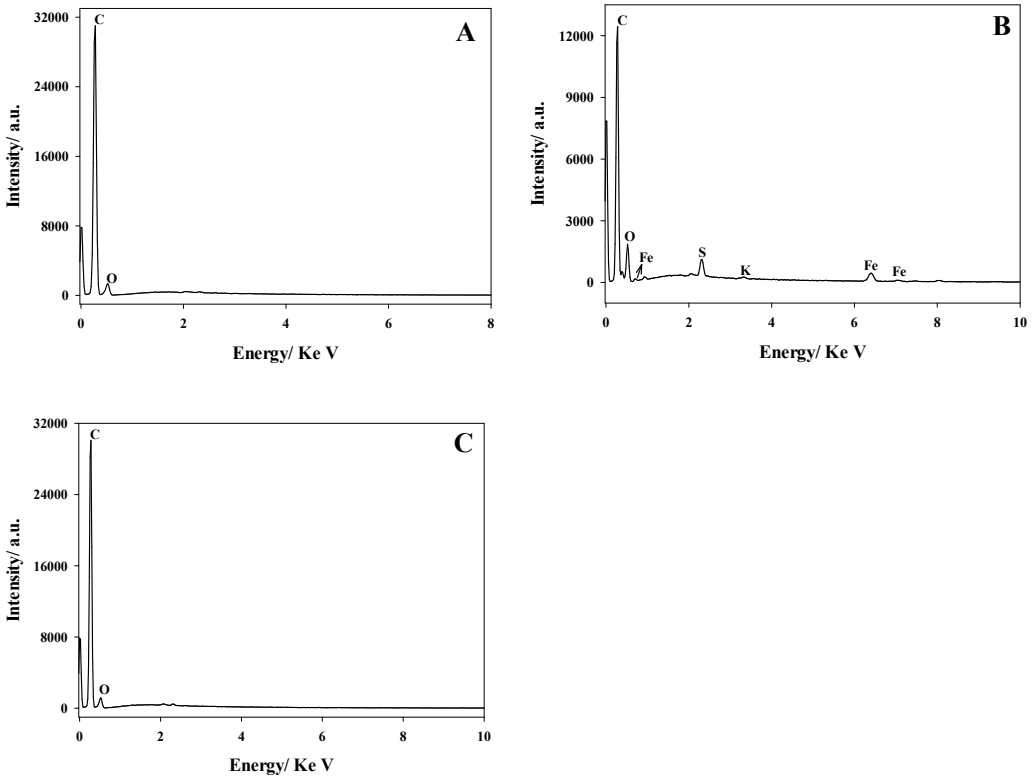

Fig. S2 EDX spectrum of bare GC (A), rGO@PB (b), P-rGO(C)

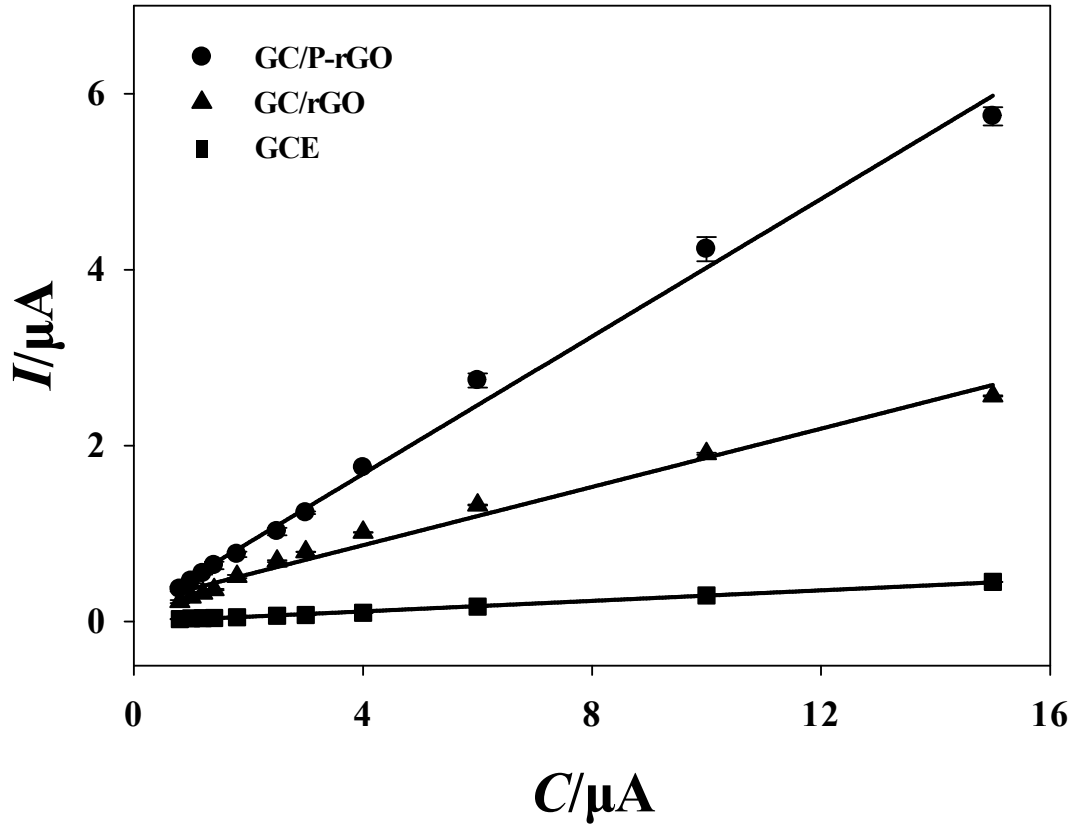

Fig. S3 Current values vs DA concentration of different modified electrode by LSV (mean ± SD, n=3).