Supplementary Information

Electrochemical Sensing of *L*-Histidine Based on Structure-Switching Aptamer and Gold Nanoparticles-Graphene Nanosheets Composites*

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Experimental Details

Reagents

L-histidine, *D*-histidine, *L*-Cystine and *L*-valine were purchased from CNS Bioservices. *tris*-(*2*-carboxyethyl) phosphine hydrochloride (TCEP) and graphite powder (325 mesh, with purity >99.99%) was obtained from Alfa Aesar. *6*-Mercapto-*1*-hexanol (MCH) was purchased from J&K Chemical Ltd. DNA was purchased from Takara Inc (Dalian). Their sequences are given below: DNA (1): 3'-CGA CTC ACT ATrA GGA AGA GAT G-5' and DNA (2): 3' -SH-$(CH_2)_6$- CAT CTC TTG ATC GGG GCT GTG CGG GTA GGA AGT AAT AGT GAG-5′-$(CH_2)_6$-Fc. All other chemicals were obtained from Beijing Chemical Co.,Ltd. and used as received.

Preparation of graphene nanosheets

In a typical procedure, all of the reagent were of analytical grade and used without further purification. Graphite oxide(GO) was synthesized from natural graphite powder by a modified Hummers method as originally presented by Kovtyukhova et al.[1] Then GO was subjected to dialysis for 7 days to completely remove metal ions and acids. Finally, the product was dried in air at room temperature. Reduction of GO was carried out by adding 3 mL hydrazine into the solution of 400 mg graphite oxide powder in 150 mL water after sonicating for 1 h and kept refluxing for 12 h at 100□. Finally, black powder of graphene-nanosheets was obtained by filtration, which was then rinsed with DI water for 6 times and dried in air at room temperature.

Preparation of gold nanoparticles-graphene nanosheets (GNPs-GNSs) nanocomposites

The synthesis of GNPs-GNSs nanocomposites was carried out in a solution phase system. First 15 mg of dried graphene nanosheets was dissolved in 85 ml of DI water by ultrasonic treatment for 30 min.Then, 5 ml of 30mM chloroauric acid solution was added to the suspension under stirring. 10 ml of 20g/L sodium citrate was introduced to the well-stirred mixture when the mixture was heated to the boiling point of water.. After refluxing for 10 min, the black precipitate was collected by centrifugation, which was then rinsed with absolute ethanol for 6 times. Finally, the products were then dried in air at room temperature for further characterization.

Preparation of the DNA duplex

The mixture of DNA(1) and DNA(2) (1 μM each) in I-B (I-B: 20mM *Tris*-HCl, pH 7.41 with 140 mM NaCl, 20 mM $MgCl_2$ and 20 mM KCl) containing 1 mM TCEP (TCEP was employed to cleave disulfides) was heated to 90□ and then slowly cooled to room temperature.

Fabrication of the aptasensor

A GCE was polished with 0.05μm alumina slurry, sonicated in deionized water, and then dried in nitrogen stream. GNPs-GNSs/GCE was made by dropping 20 μL (5mg ml^{-1}) of GNPs-GNSs colloid onto bare GCE, dried at room temperature, and thoroughly rinsed with ethanol and deionized water. The GNPs-GNSs/GCE was incubated in a 20 μL DNA duplex solution at room temperature for 20 h and then passivated by 1 mM MCH in I-B to remove non-specific aptamers.

Electrochemical detection

An electrochemical analyzer (CHI 660C, CH Instruments) was used for the electrochemical measurements. All experiments were carried out using a conventional three-electrode system consisting of a fabricated aptasensor as the working electrode, an Ag/AgCl (sat. KCl) as the reference electrode and a platinum wire as the counter electrode.

Characterizations

The structures and compositions of the as-prepared products were characterized by X-ray powder diffraction (XRD) using a Rigaku Dmax 2200 X-ray diffractometer with Cu Kα radiation (λ= 1.5416 Å). The XRD specimens were prepared by means of flattening the powder on the small slides. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) investigations were carried out by a JEOL JEM-2100F microscope. The as-prepared samples were dispersed in ethanol and dropped onto a carbon film supported on a copper grid for the drying process in air. Raman spectrometer was recorded on a LabRAM HR800(HORIBA Jobin Yvon) confocal Raman spectrometer, with an excitation laser wavelength of 514.5nm.

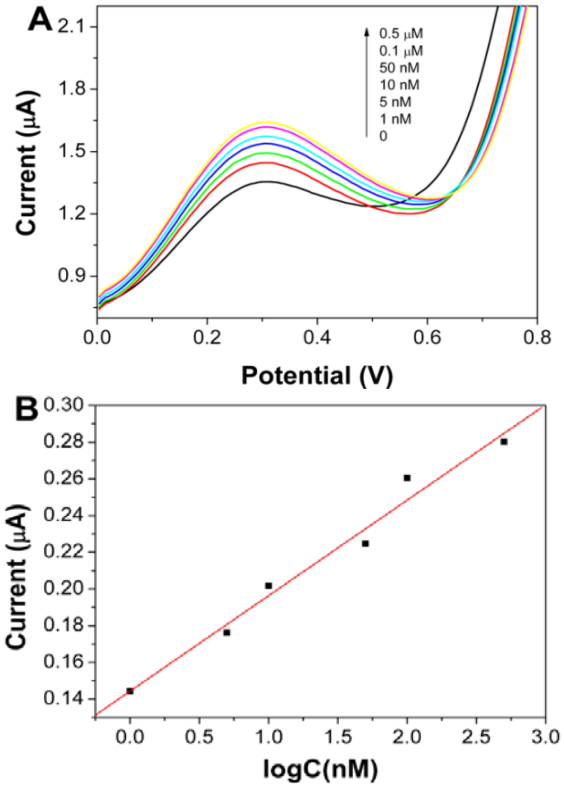

Fig. S1 A) Typical SWVs of DNAzymes/gold electrode to different *L*-histidine concentration from 1 nM to 0.5 μM. b) Linear relationship between the peak currents and L-histidine concentration.

Fig. S1 show linear detection range and detection limit of gold electrode for *L*-histidine. In comparison with gold electrode. The fabricated GNPs-GNSs/GCE electrode shows an wider linear detection range (10 pM-10 μM)and lower detection limit (0.1 pM) as compared to the linear detection range (1 nM-0.1 μM) and detection limit (1 nM) of gold electrode for *L*-histidine.

Reference

1 N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771.