Supporting information

Upconversion nanoparticles incorporated with three - dimensional graphene composites for electrocehmically sensing Baicalin from the natural plants

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Material and methods

Reagents and apparatus

Graphene oxide (GO) were purchased from Tianjin Guangfu Fine Chemical Research Institute. Yttrium (III) acetate hydrate (99.99%), ytterbium(III) acetate hydrate (99.99%), and erbium(III) acetate hydrate (99.99%) were purchased from HWRK Chem. 1-octadecene (ODE) (90%), oleic acid (OA) (90%), baicalin, sucrose (Suc), glucose (Glu), L-cysteine (L-cys), ellagic acid (Ea), $ZnCl_2$, and $MgCl_2$ were purchased from Alfa Aesar. Scutellaria baicalensis root was purchased from the local pharmacy. All reagents were of analytical grade, and used without further purification. The phosphate buffered saline (PBS) was prepared with NaH_2PO_4 and Na_2HPO_4, pH value was adjusted by using NaOH and H_3PO_4, All solutions were prepared with doubly distilled water.

Scanning electron microscope (SEM) images was obtained by SU1510 scanning electron microscope (Japan Hitachi ltd). Transmission electron microscopy (TEM) images was obtained by JEM-2100 transmission electron microscope. X-ray diffractometer (XRD) date was recorded by SmartLab 3KW (Japan Rigaku Co.). Electrochemical measurements were operated on a CHI660A electrochemical workstation (Shanghai Chenhua Instruments Co., China). The three electrode system was adopted (Work electrode: Bare GCE or modified electrode; Reference electrode: Saturated calomel electrode (SCE); Counter electrode: Platinum wire. High-purity N_2 was employed to remove oxygen for 15 min and kept over the solution during the measurements.

Preparation of $NaYF_4$: Yb, Er

The OA-UCNPs (OA-$NaYF_4$:Yb, Er) were prepared. In a typical procedure, 0.78 mmol$Y(CH_3CO_2)_3$, 0.20 mmol $Yb(CH_3CO_2)_3$ and 0.02 mmol $Er(CH_3CO_2)_3$ were mixed with 7 mL oleic acid and 15 mL 1-octadecene in a 100 mL flask. The mixture was heated to 150 ℃ under a gentle nitrogen flow and maintained at this temperature for 40 min forming a transparent colorless solution. After cooling down to 50 ℃, 10 mL methanol containing NH_4F (4.0 mmol) and sodium oleate (2.5 mmol) was slowly added into the flask and stirred for 40 min at 50 ℃. After the methanol was evaporated at 100 ℃, the solution was heated to 290 ℃ under nitrogen for 1.5 h and then cooled down to room temperature. The nanoparticles were precipitated with ethanol and washed with ethanol twice, and then redispersed in 5 mL cyclohexane.

Preparation of ligand-free $NaYF_4$: Yb, Er

The OA-UCNPs (OA-$NaYF_4$:Yb, Er) were transferred into water. Briefly, the as-prepared OA-UCNPs were ultrasonicated in a solution containing HCl (1.0 M) ($V_{water}/V_{ethanol}$ = 1:1) and kept for 30 min to remove OA from the surface of the UCNPs. The ligands-free UCNPs were then collected by centrifugation at 18,000 rpm for 20 min and further purified using an HCl/absolute ethanol solution (pH < 4.0; 0.1 M). Finally, the ligands-free UCNPs were washed with ethanol/water three times.

Results and discussion

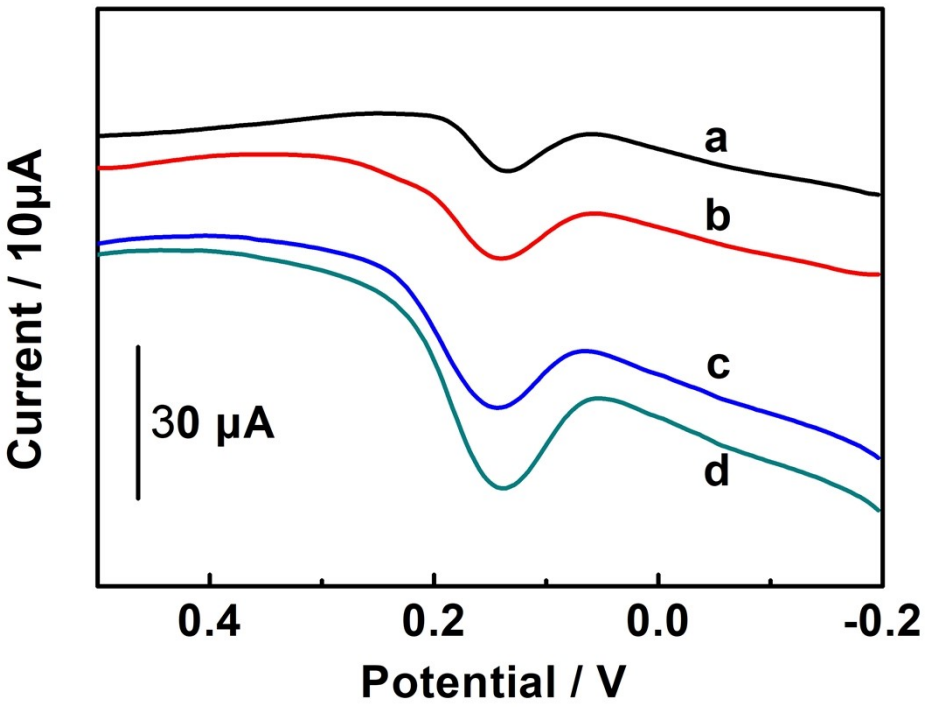

Fig. S1. The DPVs of Bn at the different electrodes surfaces: bare GCE (a), UCNPs/GCE (b), 3DG/GCE (c) and UCNPs-3DG/GCE (d) in 0.1 M PBS (pH =7.0). Pulse period of DPV: 0.2 s.

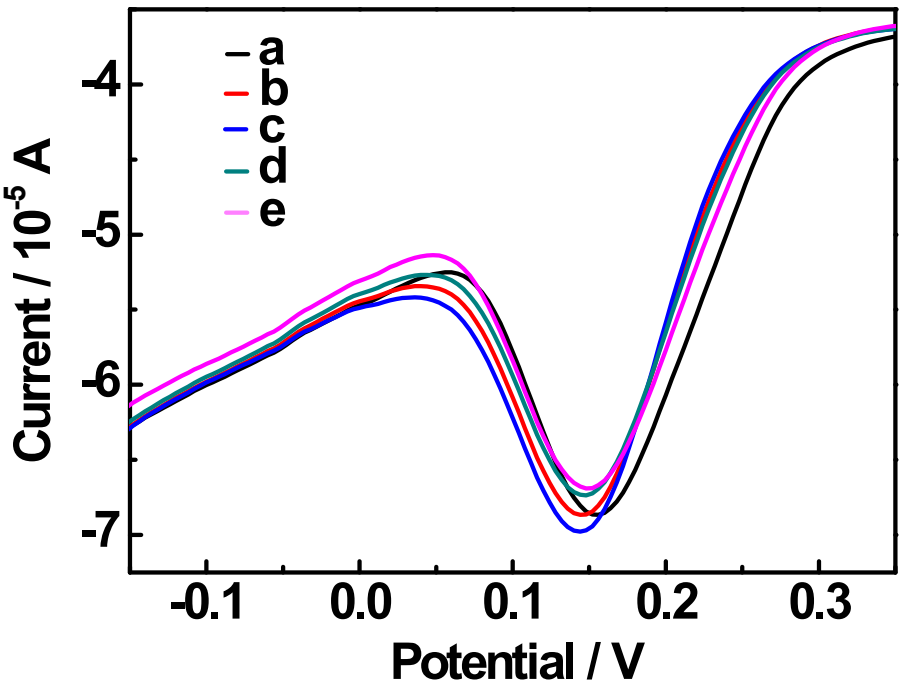

Fig. S2. The DPVs of 1.0×10^{-6} M Bn on the independently fabricating five UCNPs-3DG/GCE in 0.1 M PBS (pH 7.0), respectively.