

# Facile in situ fabrication of graphene–upconversion hybrid materials with amplified electrogenerated chemiluminescence †

Meili Yin, Li Wu, Zhenhua Li, Jinsong Ren,\* and Xiaogang Qu

*Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X*  
DOI: 10.1039/b000000x

## Experimental Section

### Materials and instrumentation

Graphite and  $\text{Ln}(\text{NO}_3)_3$  were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All chemicals were used as received from the suppliers without further purification. AFM measurements were performed by using a Nanoscope V multimode atomic force microscope (Veeco Instruments, USA). Samples for AFM images were prepared by depositing a dispersed GO/ $\text{H}_2\text{O}$  solution ( $50 \text{ mg mL}^{-1}$ ) onto a freshly cleaved mica surface and allowing them to dry in air. FTIR analy was carried out on a Bruker Vertex 70 FT-IR Spectrometer. X-ray measurements were performed on a Bruker D8 FOCUS Powder X-ray Diffractometer using Cu Ka radiation. SEM images were obtained with a Hitachi S-4800 FE-SEM. UV spectra were recorded with a JASCO-V550 spectrofluorometer. The ECL emission was detected with a Model MPI-A Electrochemiluminescence Analyzer with a conventional three-electrode system composed of a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference; working electrodes were bare Glassy carbon electrode (GCE 4 mm diameter).

### Synthesis of graphene-upconverting nanocomposites

NaOH (1.2 g, 30 mmol), water (6 mL), ethanol (12 mL), and oleic acid (15 mL) were mixed under agitation to form a homogeneous solution.  $500 \mu\text{L}$  of  $1.82 \text{ mg mL}^{-1}$  GO was added to the homogeneous solution. Then  $150 \mu\text{L}$ ,  $0.5 \text{ mol L}^{-1}$   $\text{Ln}(\text{NO}_3)_3$ , ( $\text{Ln}$ : 78 mol% $\text{Y}^{3+}$  20 mol% $\text{Yb}^{3+}$  2 mol%  $\text{Er}^{3+}$ ) aqueous solution was added under magnetic stirring. Subsequently, 1.0 M aqueous NaF (1 mL) solution was added dropwise to the above solution. The mixture was agitated for about 10 min, then transferred to a 50 mL autoclave, sealed, and hydrothermally treated at  $200^\circ\text{C}$  for 8 h. The system was cooled to room-temperature naturally, and the products were deposited at the bottom of the vessel. Pure powders could be obtained by purifying the samples with ethanol

several times to remove oleic acid, sodium oleic, and other remnants.

**Fabrication of NaYF<sub>4</sub>/Yb,Er modified glassy carbon electrode** NaYF<sub>4</sub>/Yb,Er and graphene-NaYF<sub>4</sub>/Yb,Er (25 µgmL<sup>-1</sup>) were dispersed in aqueous solution. The GCE (3 mm in diameter) was polished to a mirrorlike finish with 1.0, 0.3 and 0.05 mm alumina slurry (Beuhler) followed by a thorough rinsing with doubly distilled water. The electrodes were successively sonicated in nitric acid/acetone (1:1) and doubly distilled water, and then allowed to dry at room temperature. Subsequently, the NaYF<sub>4</sub>/Yb,Er and graphene-NaYF<sub>4</sub>/Yb,Er were dispersed on the GCE surface and allowed to dry under ambient conditions for 3 h. After the modified electrode was rinsed with doubly distilled water two or three times, a NaYF<sub>4</sub>/Yb,Er or graphene-NaYF<sub>4</sub>/Yb,Er modified GCE was obtained and used as the working electrode for ECL measurements in 0.1M PBS buffer (PH=7.4) with 100mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

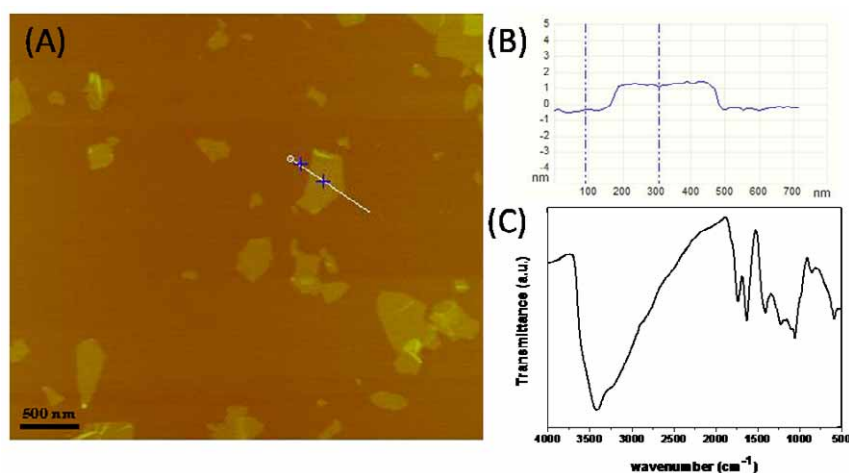


Fig. S1 (A) AFM image, (B) sectional analysis and (C) FTIR transmittance spectra of GO sheets.

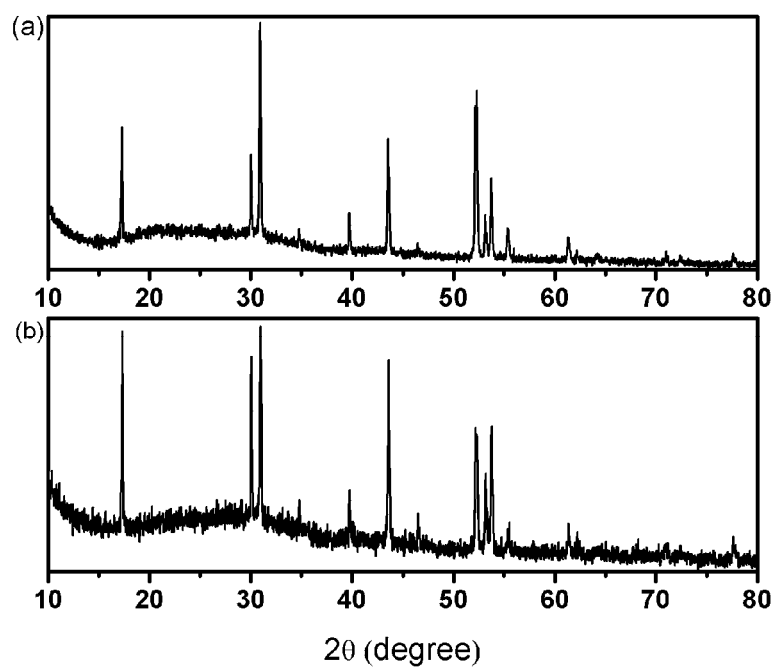


Fig. S2 XRD patterns of sample (a)  $\text{NaYF}_4/\text{Yb,Er}$  and (b)  $\text{graphene-NaYF}_4/\text{Yb,Er}$ .

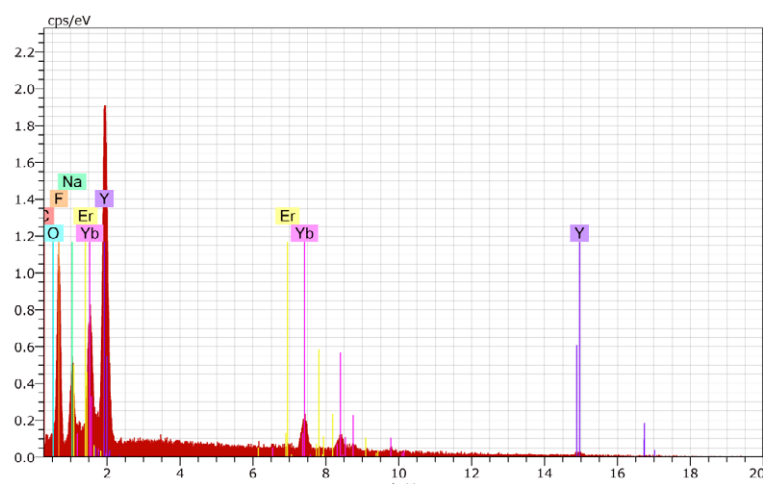


Fig. S3 The EDS spectrum of  $\text{graphene-NaYF}_4/\text{Yb,Er}$ .

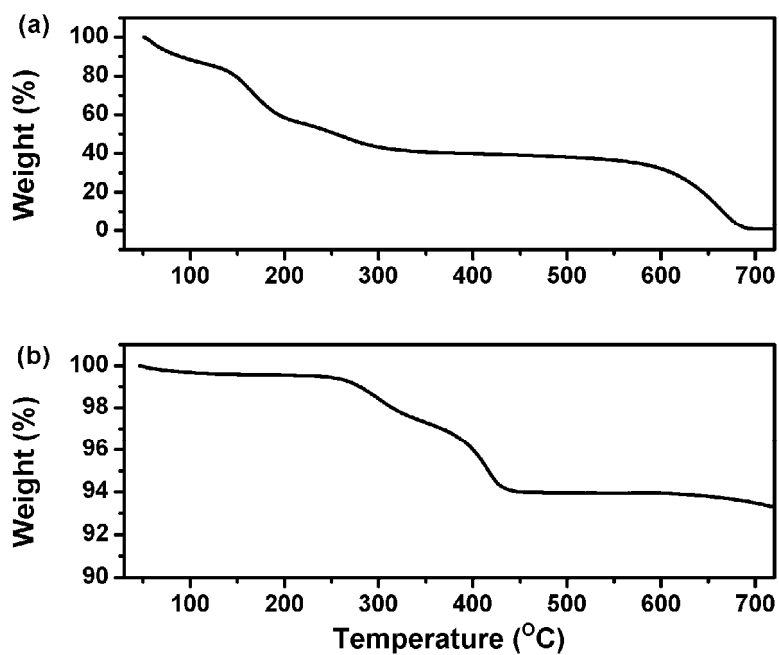


Fig. S4. TGA curves of (a) GO and (b) graphene-NaYF<sub>4</sub>/Yb,Er.

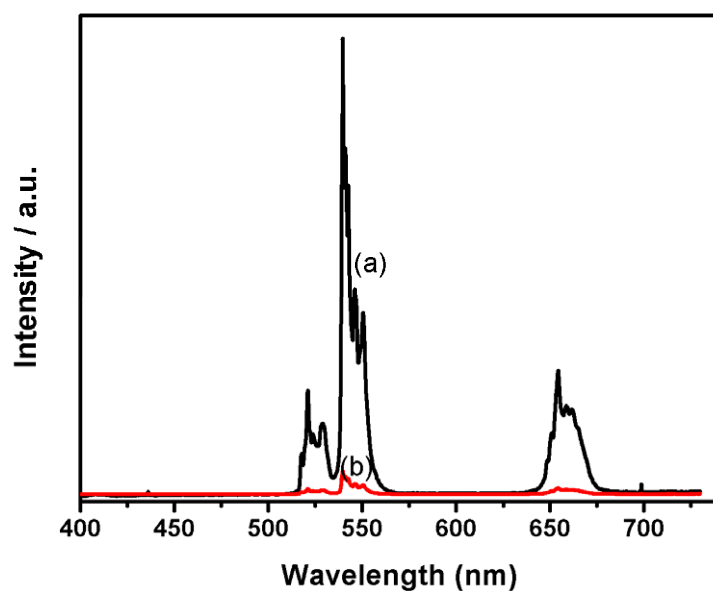


Fig. S5 Upconversion spectra of (a) NaYF<sub>4</sub>/Yb,Er and (b) graphene-NaYF<sub>4</sub>/Yb,Er, excited by a 980 nm laser diode.

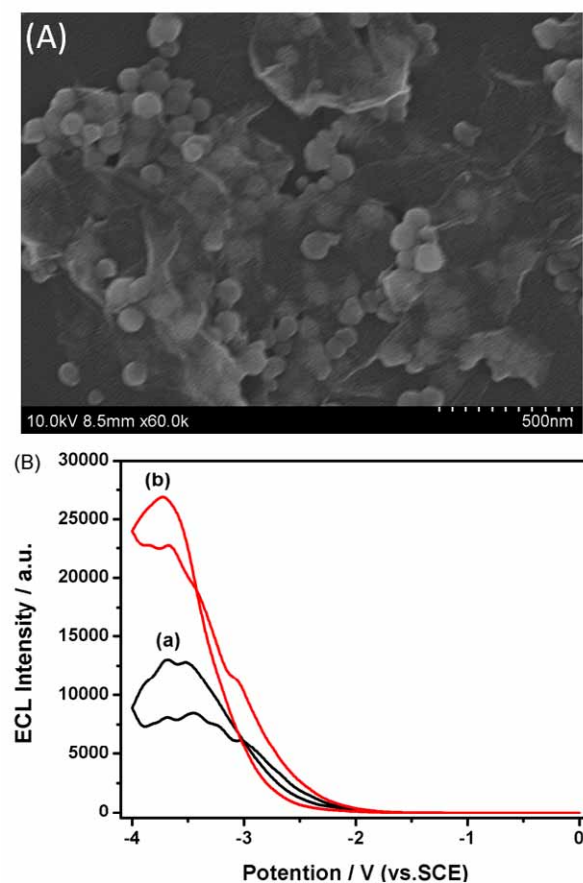


Fig. S6 Typical SEM images of the synthesized (A) graphene-NaYF<sub>4</sub>/Yb,Er spherical nanoparticles and (B)ECL–potential curves of (a) GCE-NaYF<sub>4</sub>/Yb,Er electrode and (b) GCE-graphene-NaYF<sub>4</sub>/Yb,Er electrode. Scan rate: 50 mV s<sup>-1</sup>.