Supporting Information

Organic-soluble Fluorescent Au₈ Clusters Generated from Heterophase Ligand-exchange Induced Etching of Gold Nanoparticles and Its Electrochemiluminescence

Weiwei Guo, Jipei Yuan, Erkang Wang*

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences; Graduate School of the Chinese Academy of Sciences, Changchun 130022, Jilin (P. R. China)

Experimental

Materials and preparation: Dodecylamine (DDA), 2-(Dimethylamino)ethanethiol hydrochloride (DMAET), sodium borohydrde, tetraethylammonium perchlorate (TEAP) and potassium persulfate were obtained from Aldrich Chemical (Milwaukee, WI, USA). Tetraoctylammonium bromide was purchased from Fluka (Buchs, Switzerland). Other chemicals were commercially available and at least analytical grade. All the solutions were prepared with water purified by a Milli-Q system (Millipore, Bedford, MA, USA) and stored at 4 °C.

Characterization: The photoluminescence spectra were recorded by a Perkin-Elmer LS55 Luminescence Spectrometer (Perkin-Elmer Instruments U.K.) using a 1-cm path length quartz cell at room temperature. The slot widths of the excitation and emission were set at 10.0 and 10.0 nm respectively. UV/vis absorption spectra were recorded by a CARY 500 UV/vis–near-IR Varian spectrophotometer. Transmission electron microscopy (TEM) measurements were made on a JEOL 2000 transmission electron microscope operated at an accelerating voltage of 200 kV. Samples for TEM characterization were prepared by placing a drop of gold nanoparticle solution onto a carbon-coated copper grid and then drying at room temperature.

Synthesis of DDA capped gold nanoparticles
Typically, HAuCl₄ solution (6 mL, 30 mM) was mixed with tetraoctylammonium bromide (8 mL, 50 mM) in toluene for 15 minutes. Then a freshly prepared NaBH₄ aqueous solution (6 mL, 0.3 M) was added into the above solution with vigorous stirring. After 5 minutes, 16 mg DDA was added, and the mixture was further stirred for 3 hours.

**The heterophase ligand-exchange induced etching process**

4 mL of synthesized gold NPs solution in toluene was mixed with 4 mL DMAET aqueous solution (10 mM DMAET, 5 mM citrate and 10 mM phosphate buffer pH 7.0), and the biphase mixture was stirred for 72 hours.

**Electrochemical and ECL experiments.**

Standard three-electrode system consisted of a platinum disk working electrode (3 mm), a platinum counter electrode and a silver wire as the reference electrode.

For organic phase ECL study, 10% volume ratio of gold cluster solution was added to acetonitrile solution with 20 mM tetrabutylammonium perchlorate (TEAP) as supporting electrolyte. Cyclic voltammetry experiments were performed in the potential range from -1.1 V to 1.3 V and back to -1.1 V with a scan rate of 0.1 V/s (For the control experiment, the scan rate was 0.4 V/s). The ECL signal was recorded synchronously with a single-photon counting module. In the step potential experiments, the potential pulsed between -1.1 V and 1.0 V, with the step time of 2 s.

For aqueous phase ECL study, Au NCs samples were prepared by placing a drop of Au NCs toluene solution onto the surface of Pt working electrode and then drying at room temperature. Then the Au NCs coated electrode was fixed in a three-electrode electrochemical cell containing certain volume of phosphate buffer solution (20 mM phosphate buffer, pH 8.0). Cyclic voltammetry experiments were
performed in the potential range from -1.5 V to 1.5 V and back to -1.5 V with a scan rate of 0.1 V/s. The ECL signal was recorded synchronously.

**Fig. S1** TEM image of the synthesized DDA capped gold nanoparticle precursors with a mean size of 3.7 (± 0.7) nm by calculating 200 particles.
**Fig. S2** CV spectrum (black) and ECL signal (blue) from Pt working electrode in acetonitrile solution containing 20 mM TEAP.
**Fig. S3** CV spectrum (black) and ECL signal (blue) from fluorescent gold cluster film modified Pt working electrode in 20 mM phosphate buffer (pH 8.0).