Electronic Supplementary Information on

Encoding electrochemiluminescence using $Ru(bpy)_3^{2+}$ and fluorescein isothiocyanate co-doped silica nanoparticles

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Experimental Section

Reagents. Tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate, FITC, 3-aminopropyl trimethoxysilane (APS), tripropylamine (TPA) and Triton-X100 were purchased from Sigma-Aldrich; tetraethyl orthosilicate (TEOS) was purchased from Wuhan University Silicone New Material Co. Ltd. (Wuhan, China); and indium tin oxide (ITO) sputtered glass was purchased from CBC Ings. Ltd. (Japan). All chemicals were used without further purification, and all solutions were prepared with ultra-pure water obtained from a Millipore purification system.

Synthesis of FITC doped silica nanoparticles (FITC@SiNPs). FITC@SiNPs were prepared as reported[8,11]. 40.4 mg FITC was dissolved in 5 mL anhydrous ethanol, and then 200 μL APS was added into the FITC alcohol solution with magnetic stirring. The solution was sealed in the dark and stirred for 20 h until an FITC-APS conjugate was formed. Then, a certain amount of FITC-APS solution (600, 700, 800, 900, 1000 μL) was added into a clean glass vessel and mixed with 5.3 mL anhydrous ethanol and 1.5 mL TEOS. This solution was then added into a flask containing 20 mL anhydrous ethanol, 1.59 mL 25% ammonium hydroxide and 1.63 mL ultrapure water. The mixture was stirred in the dark. After 24 h, the mixture was carefully centrifugated at 3000 rpm to remove the aggregates, and then kept at 7500 rpm to obtain the FITC@SiNPs, which were washed with ethanol, ultrapure water five times

and then dried at 4 °C in the dark.

Synthesis of RFSiNPs. RFSiNPs were synthesized using the microemulsion method[12]. A mixture of 7.5 mL cyclohexane, 1.7 mL Triton-X100, 1.8 mL n-hexanol, 480 μL 10 mM $Ru(bpy)_3^{2+}$ solution containing 20 mg well-dispersed FITC@SiNPs, 100 μL TEOS and 60 μL 25% ammonium hydroxide was stirred for 24 h in the dark, and then 2 mL acetone was added into the mixture to precipitate the RFSiNPs. The mixture was centrifugated at 7500 rpm to obtain the RFSiNPs, which were then washed with acetone, ethanol and water in sequence and dried at 4 °C in the dark before use.

Preparation of ITO modified electrodes. An ITO electrode was cleaned using ethanol and water, dipped into a fixed aliquot of 10 mg/mL RFSiNPs ethanol solution in order to prepare the modified electrode (RFSiNPs@ITO), and then dried in a sealed case at room temperature. Before the experiment, a piece of copper adhesive tape was attached onto the electrode surface and then covered with waterproof adhesive tape.

Electrochemical experiments. ECL encoding experiments were carried out in a three-electrode system using the RFSiNPs@ITO electrode as the working electrode, a silver wire as the reference electrode and a platinum wire as the counter electrode. Potential control was achieved using a CHI 660b (Shanghai, China). The applied potential was selected from 0 to 1.3 V and then to 0 at a scan rate of 40 mV/s for colorimetric experiments[9] or fixed at 1.3 V for the ECL encoding experiment. The electrolyte solution was 0.1 M phosphorus buffer solution (PBS, pH 7.0) containing 10 mM TPA. The electrochemical cell was a fluorescence cuvette. The ECL intensity was measured using an F-4500 fluorometer (Hitachi, Japan) with the emission grating at 20 nm and at a negative high voltage of -950 V. The color pictures were taken using a Nikon D300 CCD camera (Japan), setting the ISO at 3200, the white balance at 5880 K, and the shutter time at 1/1.3s.

For the encoding experiment, a F-4500 fluorometer (Hitachi, Japan) was used as a detector for the fluorescence signal. The excitation and emission gratings were set at 1 nm and 20 nm, and the negative high voltage was set at -950 V. An excitation wavelength of 460 nm was selected.

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Apparatus. Transmission electron microscopy (TEM) images were obtained using a TECNAI F-30 (Netherlands), and scanning electron microscopy (SEM) images were taken using LEO1530 (German).

Supporting Figures:

Figure S1

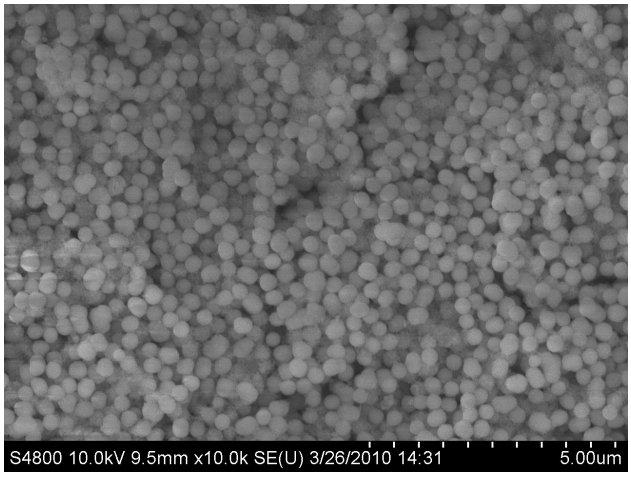

Figure S1. SEM image of FITC@SiNPs.

Figure S2

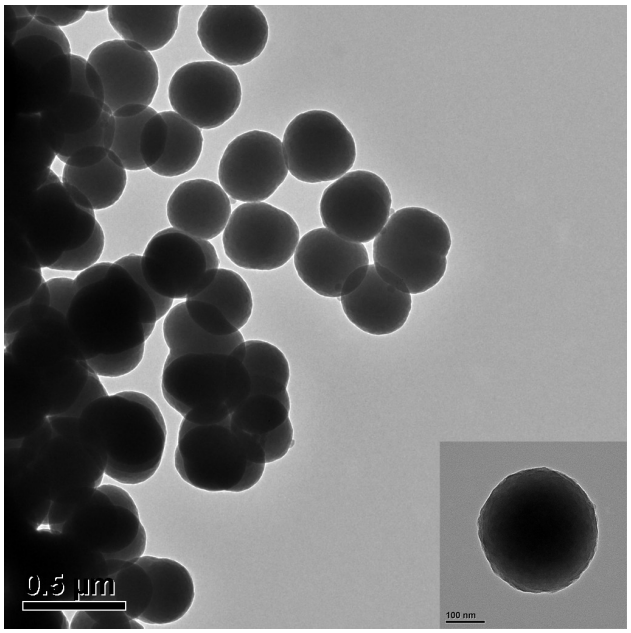

Figure S2. TEM images of RFSiNPs.