Supplementary Information

Multifunctional Polyoxometalates-Modified Upconversion Nanoparticles: Integration of Electrochromic Devices and Antioxidants Detection

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1. EXPERIMENTAL SECTION

1.1 Materials The rare-earth oxides Yb_2O_3, Er_2O_3, and Tm_2O_3 (purity>99.99%) were obtained from the Changchun Hepalink rare-earth materials company. Oleic acid and octadecene were purchased from Sigma-Aldrich. Poly(diallyldimethylammonium chloride) (PDDA) and poly(allylamine hydrochloride) (PAH) were obtained from Sigma. 1-octadecene (ODE, 90%), oleic acid (OA, 90%), polyoxyethylene (5) nonylphenyl ether (Igepal CO-520), tetraethyl orthosilicate (TEOS), ethylenediaminetetraactic acid disodium salt (EDTA) and 3-aminopropyltriethoxysilane (APTES) were purchased from Aldrich. 1-hexanol, cyclohexane, $Na_2WO_4.2H_2O$ and ammonium hydroxide (25-28 wt %) were purchased from Beijing Chemical Reagent Company (Beijing, China). Other chemicals were of analytical grade and used as received without further purification. Acetate buffer solution (pH = 4.5) containing 0.1 M NaAc and 0.1 M HAc was used as the electrolyte throughout the experiments. Water used throughout all experiments was purified with a Millipore system.

1.2 Apparatus Transmission electron microscope (TEM) images were obtained with a TECNAI G2 high-resolution TEM operating at 200 kV. Absorption measurements were performed on a Cary 500 UV vis NIR spectrometer (Varian). Luminescence measurements were measured on a Photon Technology International (PTI) Time master fluorescence lifetime spectrometer equipped with GL-302 dye laser pumped by PTI GL-3300 nitrogen laser and a GL-303 frequency doubler. Spectroelectrochemical measurements (in situ luminescence) were carried out in a modified luminescence cell. The electrochemical experiments were conducted with a CHI 832C electrochemical workstation (Shanghai Chenhua Instrument Corporation, China). The substrates were commercial conducting indium tin oxide (ITO, surface resistance <20 Ω/square) with a geometric area of ~1 cm×5 cm purchased from Nanbo Display Technology Co., Ltd. (Shenzhen, China).

1.3 Synthesis of hydrophilic and OA-stabilized UCNPs: The hydrophilic UCNPs were prepared according to the literature.[1] A total 4mL of $Y(NO_3)_3$, $Yb(NO_3)_3$, and $Er(NO_3)_3$ (0.2 M) (molar ratio, Y/Yb/Er = 80:18:2) was added into 0.8 mmol of EDTA solution and stirred for 1 h. Then, 12 mL of NaF aqueous solution (0.8 M) was added into the above solution and stirred for another 1 h. The as-obtained mixing solution was transferred into a Teflon bottle, and maintained at 180 ^{0}C for 2 h. After cooled to room temperature, the precipitates were separated by centrifugation and washed several times with deionized water and ethanol and then dried in air.

Yb_2O_3, Er_2O_3, and Y_2O_3 were separately dissolved in excess 1:1 hydrochloric acid aqueous solution at 80 ^{0}C. After the hydrochloric acid and water evaporated at 140^{0}C, the resulting powders were redispersed in water to yield the $YbCl_3$ (0.4 M), $ErCl_3$ (0.2 M), and YCl_3 (0.4 M) aqueous stock solutions. OA-stabilized UCNPs were prepared according to the literature.[2] Typically, YCl_3 (3 mL), $YbCl_3$ (0.675mL) and $ErCl_3$ (0.15 mL) aqueous solution were injected in a 50 mL flask. After removal of the water, 15 mL oleic acid and 22.5 mL octadecene were added, and the solution was heated to 160 °C to form a homogeneous solution, and then cooled down to room temperature. Subsequently, methanol solution (15 mL) containing NH_4F (0.224 g) and NaOH (0.15

g) were slowly added into the flask. After vigorous stirring for 30 min, the solution was slowly heated to 220^0C to remove the residual water and impurities with low boiling point under Ar protection. Thereafter, the temperature was increased to 300^0C at a rate of 10^0C min^{-1} and remained at this temperature for 1.5 h. After the solution was cooled naturally, the nanoparticles were obtained from the solution with ethanol, and washed with ethanol/water (1:1 v/v) for three times, and finally redispersed in cyclohexane.

1.4 Synthesis of $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}].5H_2O$-coated $NaYF_4$: $Yb^{3+}/Er^{3+}@SiO_2$ nanoparticles (UCNPs@Na-POMs)

The mixture solution of UCNPs cyclohexane solution (4 mL, 0.01 M), CO-520 (0.1 mL), and cyclohexane (6 mL) in a flask was stirred for 10 min, then CO-520 (0.4 mL) and ammonia (0.08 mL) were added and the container was sealed and sonicated for 20 min to form a transparent emulsion. The solution was stirred for one day after adding TEOS (0.04 mL). Silica/$NaYF_4$ nanospheres were isolated by acetone, followed by centrifuging and washing with ethanol and water several times to remove surfactant molecules. Finally, the obtained UCNPs were modified with 3-aminopropyltriethoxysilane (APTES) stirring for 24 h, and then added into Na-POMs solution (0.01 mM) prepared according to the previous report for 3 h. After centrifuging, these UCNPs/Na-POMs were suspended in 10 mL deionized water by ultrasonication for the further experiments.

1.5 Preparation of PAH/UCNPs@Na-POMs/PDDA film on the ITO Electrode

Before modification, ITO slides were washed with acetone, ethanol and 1 M sodium hydroxide solution (H_2O: ethanol 1:1, v/v) for 15 min ultrasonic bath successively, and finally rinsed with pure water and dried under N_2 flow. The chips were dipped in PAH aqueous solution (5 mg/mL) for 15 min, then rinsed with water several times to remove the physically adsorbed PAH, and dried under N_2 flow. After that, ITO/PAH modified electrodes were dipped into 5 mM UCNPs@Na-POMs solution for 30 min and then 2 μL PDDA (0.5 mg/mL) was cast on the surface to fabricate PAH/UCNPs@Na-POMs/PDDA film.

2. FIGURE

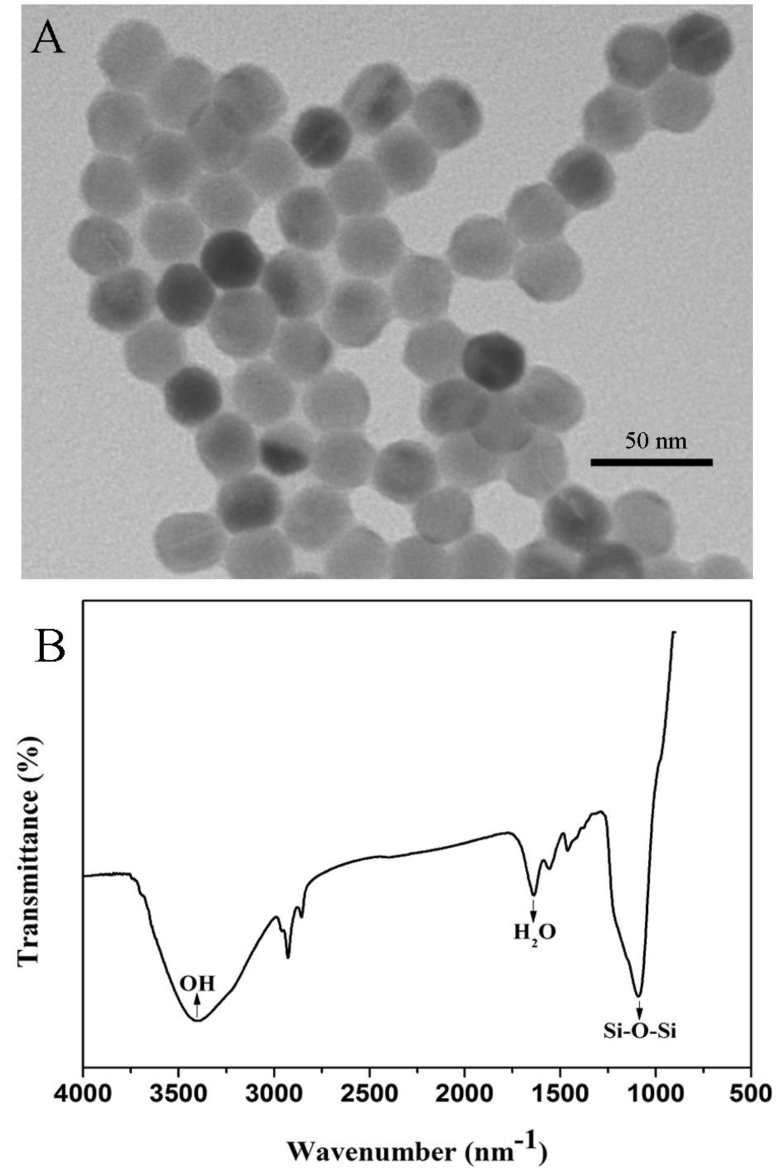

Fig. S1. TEM (A) and FTIR (B) spectra of $NaYF_4$: $Yb^{3+}/Er^{3+}@SiO_2$.

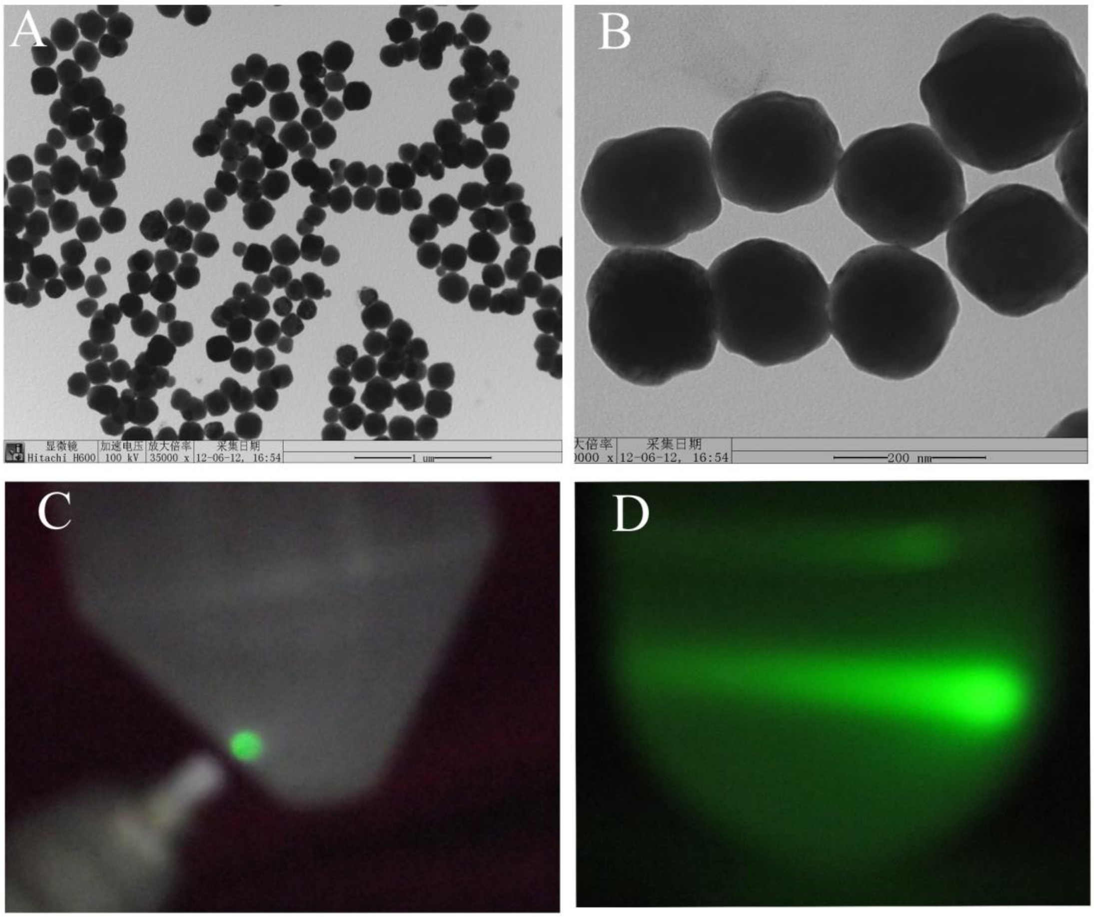

Fig. S2 TEM (A) and high-resolution TEM (B) images of hydrophilic UCNPs; The upconversion luminescence photograph of hydrophilic (C) and OA-stabilized (D) UCNPs under excitation at 980 nm.

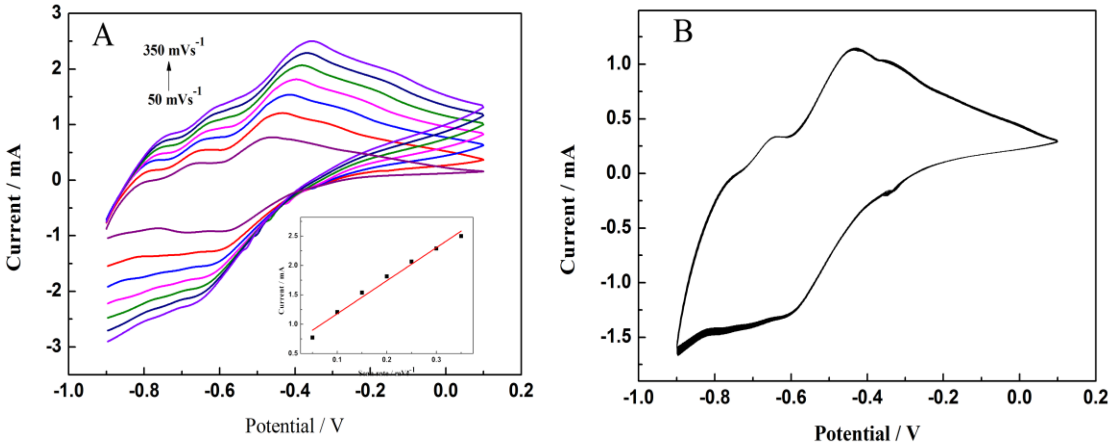

Fig. S3 (A) Cyclic voltammograms (CVs) of ITO/PAH/UCNPs@Na-POMs/PDDA electrode at different scan rates (from inner to outer): 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 v/s. Inset: plot of peak current (Ip) vs. scan rate; (B) 100 consecutive CVs of the prepared electrode at 100 mVs^{-1} in 0.1 M HAc-NaAc buffer solution (pH = 4.5).

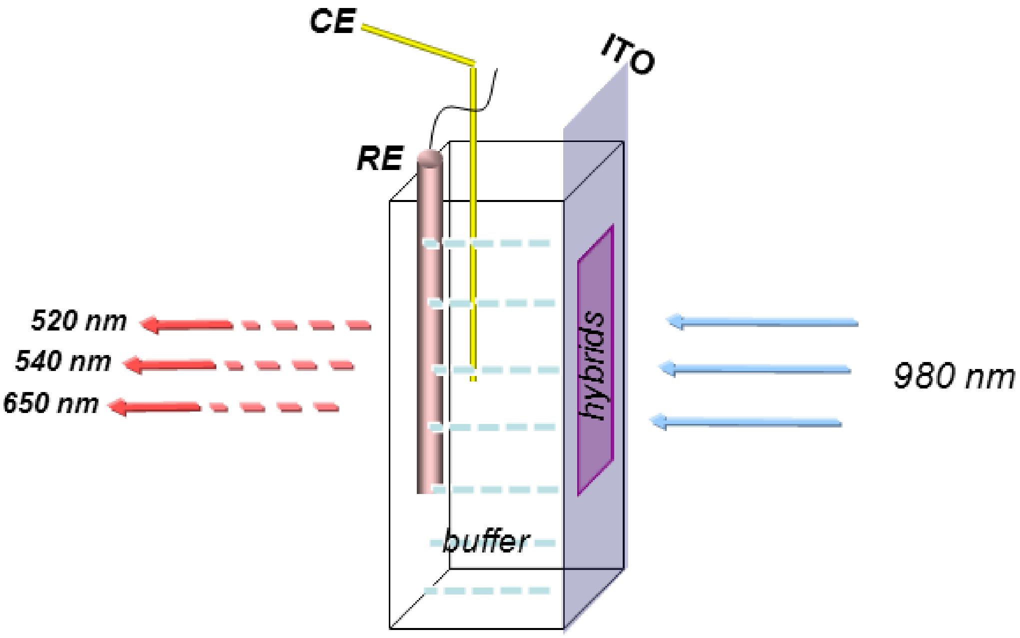

Fig. S4 Schematic representation of fluorescence spectroelectrochemical cell

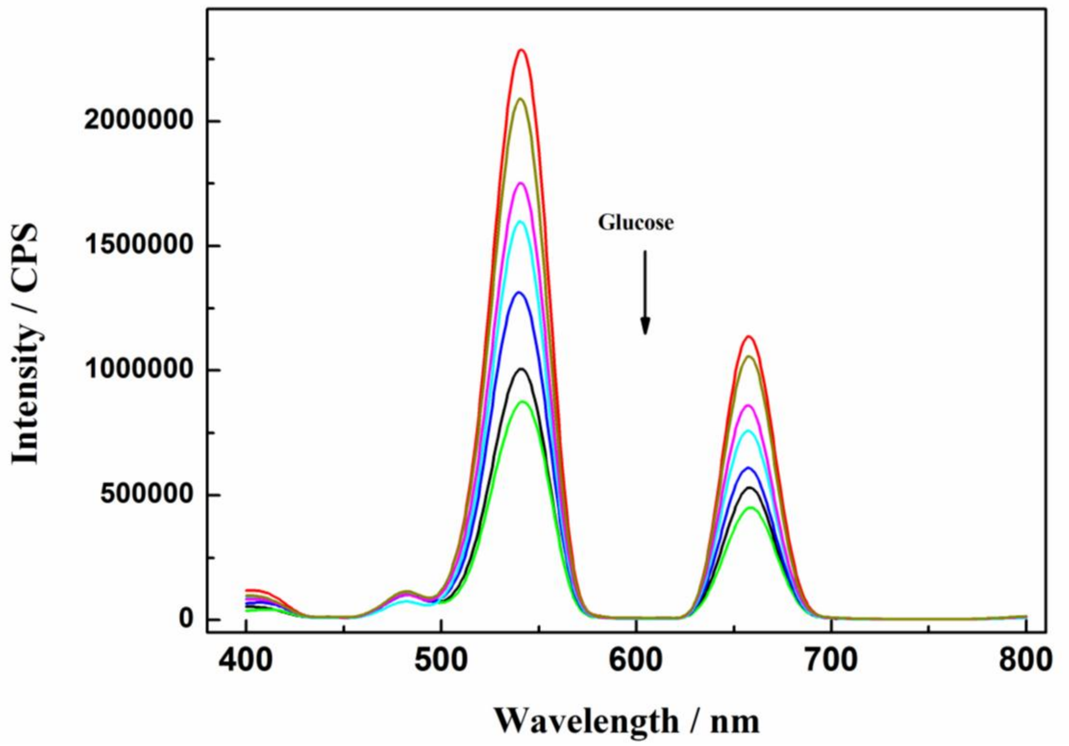

Fig. S5 Photoluminescence response of POM-modified $NaYF_4$:Yb/Er@SiO_2 as a function of glucose concentration (0, 1, 3, 5, 10, 20, 40 mM) in an aqueous solution.

References:

1. Dai, Y.; Ma, P.; Lin, J. *ACS Nano* **2012,** *6*, 3327–3338.
2. Li, Z.; Zhang, Y.; Jiang, S. *Adv. Mater.* **2008,** *20*, 4765-4769.