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$_2$O$_3$, Er$_2$O$_3$, and Tm$_2$O$_3$ (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), ethylenediaminetetraacetic acid disodium salt (EDTA) and 3-aminopropyltriethoxysilane (APTES) were purchased from Aldrich. 1-hexanol, cyclohexane, Na$_2$WO$_4$.2H$_2$O 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 °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$_2$O$_3$, Er$_2$O$_3$, and Y$_2$O$_3$ were separately dissolved in excess 1:1 hydrochloric acid aqueous solution at 80 °C. After the hydrochloric acid and water evaporated at 140°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$_4$F (0.224 g) and NaOH (0.15 g) was added to the solution, and the mixture was stirred for another 1 h. After being cooled to room temperature, the solution was centrifuged and washed several times with methanol and then dried in air.
g) were slowly added into the flask. After vigorous stirring for 30 min, the solution was slowly heated to 220°C to remove the residual water and impurities with low boiling point under Ar protection. Thereafter, the temperature was increased to 300°C at a rate of 10°C 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 NaYF₄: Yb³⁺/Er³⁺@SiO₂ 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/NaYF₄ 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 (H₂O: ethanol 1:1, v/v) for 15 min ultrasonic bath successively, and finally rinsed with pure water and dried under N₂ 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 N₂ 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

![TEM and FTIR spectra of NaYF₄: Yb⁴⁺/Er⁵⁺ @ SiO₂](image)

**Fig. S1.** TEM (A) and FTIR (B) spectra of NaYF₄: Yb⁴⁺/Er⁵⁺ @ SiO₂.
**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 NaYF₄:Yb/Er@SiO₂ as a function of glucose concentration (0, 1, 3, 5, 10, 20, 40 mM) in an aqueous solution.

References:
