Supplementary Information

Polyoxometalate-based Inorganic-Organic Hybrid Film Structure with Reversible Electroswitchable Fluorescence Property

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Experimental Section

Materials:

The tungstophosphate $K_6[P_2W_{18}O_{62}]\cdot 14H_2O$ (P_2W_{18}) was prepared according to the literature method. [1-2] Poly(styrenesulfonate) (PSS), poly(allylamine hydrochloride)(PAH), 3-aminopropyltriethoxysilane(APTES), rhodamine B isothiocyanate and triton X-100 were purchased from Sigma. Tetraethylorthosilicate (TEOS) was obtained from Beijing Yili Chemical Reagent Factory (Beijing, China). 1-hexanol, cyclohexane, and ammonium hydroxide (25–28 wt.%) were purchased from Beijing Chemical Reagent Company (Beijing, China). All other chemicals were of analytical grade. All aqueous solutions were prepared with ultrapure water (>18 MΩ). 0.1 M HAc–NaAc buffer solution (pH=4.5) was used as the electrolyte throughout the experiments.

Instrumentation:

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Electrochemical experiments were conducted with a CHI832 electrochemical workstation (Shanghai Chenhua Instrument Corporation, China). Fluorescence measurements were carried out on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc., France) with excitation and emission slit widths of 5 nm. Absorption measurements were performed on a Cary 500 UV-vis spectrometer (Varian). Scanning electron microscopy (SEM) images were determined with a Philips XL-30 ESEM. The size of DSNPs was measured using the JEOL 2010 transmission electron microscope (TEM) operated at an accelerating voltage of 200 kV. Photoluminescence decay was 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. The ITO plates (surface resistance of 30-60 Ω/cm^2) with a geometric area of ~1 cm×5 cm were purchased from Nanbo Display Technology Co., Ltd. (Shenzhen, China).

Synthesis of rhodamine B isothiocyanate-doped silica nanoparticles(DSNPs):

According to previous report 3, rhodamine B isothiocyanate was firstly linked to the coupling agent APTES by a reaction of rhodamine B isothiocyanate (0.5 mg) and APTES (50 μL) in 1-hexanol (2.5 mL) of under N2 protection. Next, 0.4 mL of the resulting APTES–rhodamine B isothiocyanate conjugates was added to the water/oil (W/O) microemulsion solution containing cyclohexane (7.5 mL), 1-hexanol (1.6 mL), Triton X-100 (1.77 g), and deionized water (480 μL), and stirred for 15 min. TEOS (50 μL) was then added. After stirring for another 30 min, the hydrolysis of TEOS and rhodamine B isothiocyanate–APTES was initiated by the addition of NH4OH (60 μL), and the mixture was stirred for 24 h. The final surface layer incorporating primary amines was formed by adding APTES (50 μL) and stirring for 24 h. Finally, the as-prepared DSNPs were centrifuged and washed four times with ethanol and three times with deionized water, then diluted in 8 mL deionized water for the future using. The nanoparticles were uniform in size, 25 nm in diameter, as characterized by transmission electron microscopy (TEM) images." could be deleted.

Preparation of $\{(PSS/DSNPs)_3/PSS/(PAH/P_2W_{18})_2\}$ film on the ITO Electrode:

Before modification, the ITO chips were washed with acetone, ethanol, and water in an ultrasonic bath sequentially. Then ITO chips were immersed in a solution of 1:1 (v/v) ethanol/NaOH (1 M) for 15 min to activate the surface. After being rinsed with pure water, the chips were dipped in a 5 mg/mL PAH aqueous solution (pH 2.0) for 20 min to modify a monolayer of PAH. The modified substrates were rinsed with water several times to remove the physically adsorbed PAH, and dried under a stream of nitrogen. Then, 50 μL 0.5 mg/mL PSS solution, DSNPs solution, 0.5 mg/mL PAH solution and 5 mM P_2W_{18} solution were pipetted and dropped respectively on the modified ITO chip, following spin-coating at 1500 rpm for 30 s to fabricate the hybrid film structure.

Spectroelectrochemical Experiments:

Spectroelectrochemical measurements (in situ fluorescence) were carried out in a modified fluorescence cell according to the previous report (1 cm length quartz cell) at room temperature (Fig. S5). [4] The cell was capped with a Teflon plate, which was also served as the electrode support. ITO electrode, platinum wire, and Ag/AgCl (saturated KCl) were used as the working electrode, the counter electrode, and the reference electrode, respectively.

A rough estimation of the relative quantum yield of the present fluorescence switching system was calculated by using Rhodamine B solution as a reference. The detailed calculation process was described as follows:

A 0.25 μg/mL Rhodamine B ethanol solution (quantum yield(Φ)=0.9) was selected as the reference. The Φ is calculated with the equation:

$\Phi x=\Phi r(nx/nr)^2(Ar/Ax)(Dx/Dr)$ [5]

n is the average refractive index of the solution, D is the integrated area under the corrected emission spectrum, and A is the absorbance/cm of the solution at the excitation wavelength. Subscripts x and r refer to the switching system and reference solution, respectively.

The related fluorescence data of the two switching states were collected upon excitation at 540 nm. Finally, the probable relative quantum yields for the fluorescence switching at “ON” and “OFF” states were calculated to be 0.183 and

0.007, respectively.

Figure

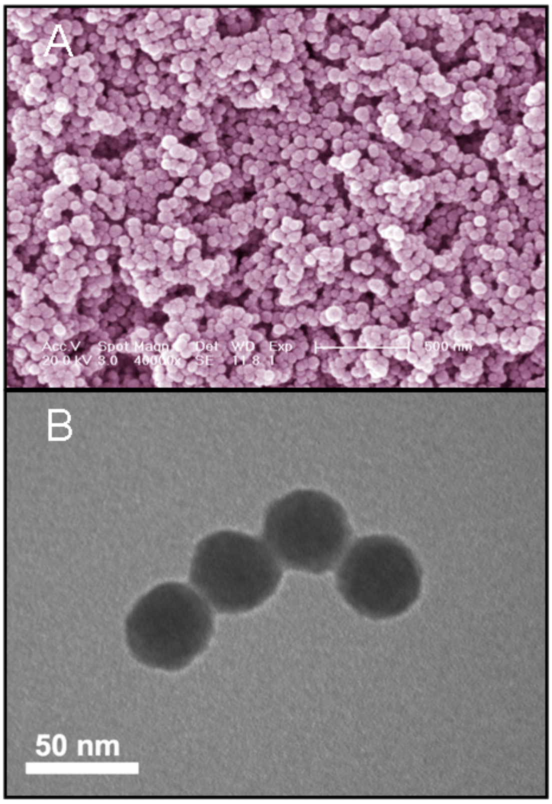

Fig. S1 (A) Scanning electron microscopy images of the synthesized dye-doped silica nanoparticles (DSNPs). ***(B)*** Transmission electron microscopy (TEM) image of the synthesized (DSNPs).

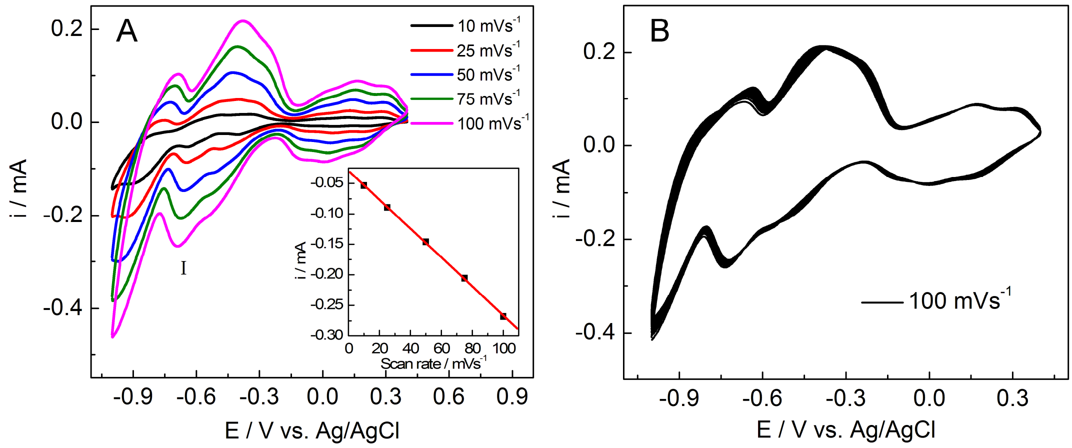

Fig. S2 (A) Cyclic voltammograms at different scan rates (10, 25, 50, 75, 100 mVs^{-1}) of the as-prepared {$(PSS/DSNPs)_3/PSS/(PAH/P_2W_{18})_2$} hybrid film on an ITO substrate. Inset: Plots of reduction peak current I versus the scan rate. ***(B)*** 100 consecutive cyclic voltammogram cycles of the {(PSS/DSNPs)$_3$/PSS/(PAH/P$_2$W$_{18}$)$_2$} hybrid film at 100 mVs^{-1}.

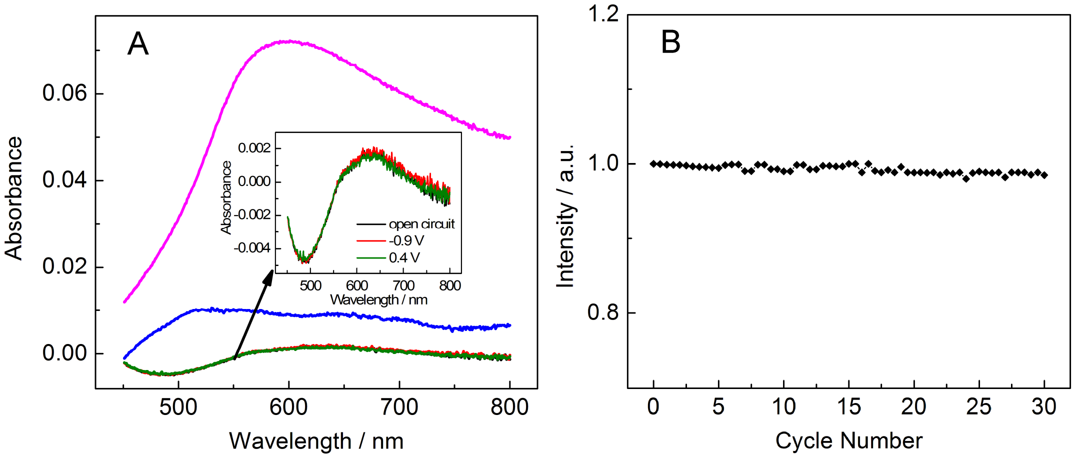

Fig. S3 (A) Absorption spectrum of as-prepared {(PSS/DSNPs)$_3$/PSS/(PAH/P$_2$W$_{18}$)$_2$} hybrid film on ITO electrode under open circuit (blue line) and at applied potential of -0.9 V (pink line) and absorption spectrum of [PSS/DSNPs]$_3$ under open circuit (black line), at applied potential of -0.9 V (red line) and at applied potential of 0.4 V (green line).The Inset shows the detail information of the absorption spectrum of [PSS/DSNPs]$_3$ under different conditions. ***(B)*** Normalized fluorescence intensity of [PSS/DSNPs]$_3$ film in the redox potential cycles as a function of cycle number.

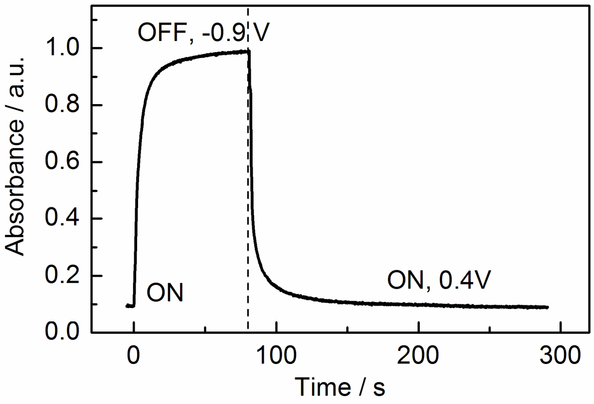

Fig. S4 Normalized absorbance against time for the hybrid film on application of -0.9 V (OFF state) and 0.4 V (ON state) to the ITO-functionalized substrate.

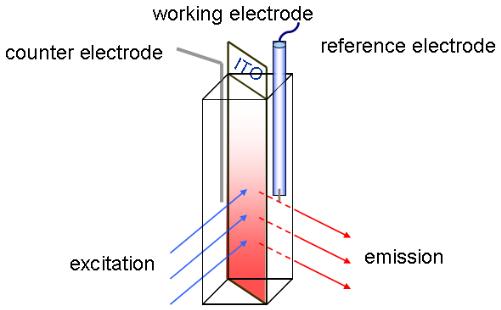

Fig. S5 Schematic representation of fluorescence spectroelectrochemical cell

Reference

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