Supplementary Information

Gold Nanocluster -based Electrochemically Controlled Fluorescence Switch Surface with Prussian Blue as the Electrical Signal Receptor

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1. Experimental Section

1.1 Materials.

$HAuCl_4 \cdot 3H_2O$, KCl, HCl, $K_3[Fe(CN)_6]$, $FeCl_3$, NaOH were bought from Beijing Reagent Company. Bovine serum albumin (BSA, fraction V) and chitosan (low molecular weight) were obtained from Sigma-Aldrich. All other chemicals were of analytical grade. All aqueous solutions were prepared with ultrapure water (>18 MΩ).

1.2 Instrumentation.

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. [1] 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. The ITO plates (surface resistance of 30-60 Ω/cm^2) were purchased from Nanbo Display Technology Co., Ltd. (Shenzhen, China).

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Electrochemical experiments were conducted with 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 3 nm and 4 nm, respectively. Absorption measurements were performed on a Cary 500 UV-Vis-NIR spectrometer (Varian). The size of Au nanocluster 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. A laboratory U.V lamp (365 nm, 8.0 W) was placed in front of the sample for fluorescence testing, and pictures were taken at regular intervals during the cycling of the multilayer surface.

1.3 Preparation PB/Au nanoclusters-chitosan multilayer structure surface

1.3.1 Synthesis of BSA-Au nanoclusters

All glassware used in the experiment was cleaned in a bath of freshly prepared 3:1 HCl/HNO_3 and rinsed thoroughly in water prior to use. Au nanoclusters were prepared following previous method. Typically, 5 mL aqueous $HAuCl_4$ solution (10 mM, 37 °C) was added to BSA solution (5 mL, 50 mg/mL, 37 °C) under vigorous stirring. 0.5 mL 1 M NaOH solution was then introduced, and the mixture was incubated at 37 °C for 24 h. The solution was then dialyzed in double distilled water for 48 h to remove unreacted $HAuCl_4$ or NaOH. The final solution was stored at 4 ℃ when not in use. Herein, the concentration of the BSA in Au nanoclusters was adopted to confirm the concentration of Au nanoclusters in the following experiments. The concentration 3.96×10^{-4} M was measured by spectrophotometry using a molar absorptivity of 44,000 M^{-1} cm^{-1} at 278 nm.

1.3.2 Preparation of PB layer, Au nanoclusters-chitosan layer and

PB/Au nanoclusters-chitosan multilayer on ITO electrode.

Before modification, the ITO chips were washed with acetone, ethanol, and water in ultrasonic bath sequentially. Then ITO chips were immersed in a solution of 1:1 (v/v) ethanol/NaOH (1 M) for 15 min to active the surface. After rinsed with pure water and dried under N_2 flow, the ITO electrodes were electropolymerizated with PB in a freshly prepared solution containing 0.1 M KCl, 0.1 M HCl, 2.5 mM $K_3[Fe(CN)_6]$, and 2.5 mM $FeCl_3$ by applying a controlled potential of 0.4 V for 480 s. The obvious color and absorbance change were conformed the successful preparation of the PB film. The modified electrode was thoroughly rinsed with water to remove the physically adsorbed species, and then dried in 100℃ over night.

1% chitosan solution was prepared by dissolution 0.1g chitosan in 10 mL 1% acetic acid. Then 10 mL treated Au nanoclusters solution was added and mixed together to form a homogeneous mixed solution. The Au nanoclusters-chitosan fluorescent layer was fabricated by dropping 80 μL mixed solution on the ITO electrode or PB surface two times by the spin-coating technique at 500 rpm for 120 s. The thickness of the prepared multilayer structure surface PB/Au nanoclusters-chitosan was determined by Dektak 6M Stylus Surface Profilometer, which can give profile data of a sample detecting the vertical detection of a stylus in contact with the sample which is moved horizontally across the sample surface. The average thickness was measured to be ca. 1080-1260 nm.

According to Laviron's treatment, [2-3] the electrochemical rate constant K_s of the multilayer can be determined in a straightforward manner from equations (1) and (2).

$$E_{pc} = E^{o'} - (RT/\alpha nF)Ln(\alpha nFv/RTK_s) \quad (1)$$

$$E_{pa} = E^{o'} + [RT/(1-\alpha)nF]Ln[(1-\alpha)nFv/RTK_s] \quad (2)$$

where α is charge transfer coefficient, F is Faraday number[C/mol], K_s is heterogeneous electron transfer rate constant, n is number of electrons transferred in the reaction, R is gas universal coefficient [J/(K mol)], v is CV potential sweep rate [V/s], and T is solution temperature [K]. Assuming that the product αn does not vary with potential, the graphs of E_c−ln(v) and E_a−ln(v) have been fitted with linear

regression lines, as shown in the inset figure in Fig. S6. The respective slopes of the lines are $RT/(\alpha nF)$ and $RT/((1-\alpha)nF)$. The values of αn and $(1-\alpha)n$ were thus obtained and substituted back in equations (1) and (2) to solve K_s. The rate constant $K_s=(0.062\pm0.014)\ s^{-1}$ is obtained.

2. Figure

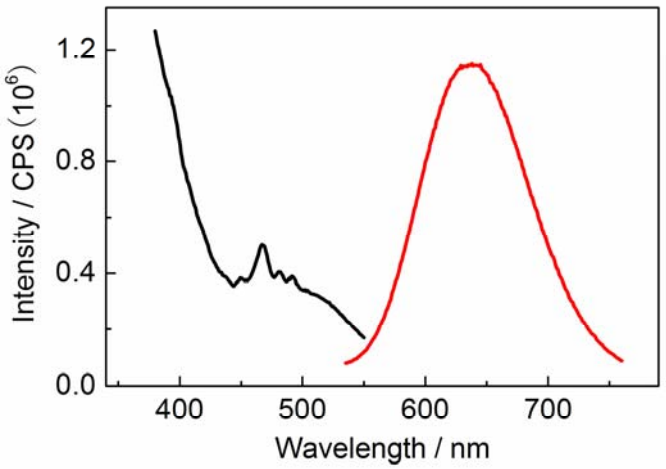

Fig.S1 The excitation (red line) and emission (black line) fluorescence spectra of as-prepared BSA-Au nanoclusters.

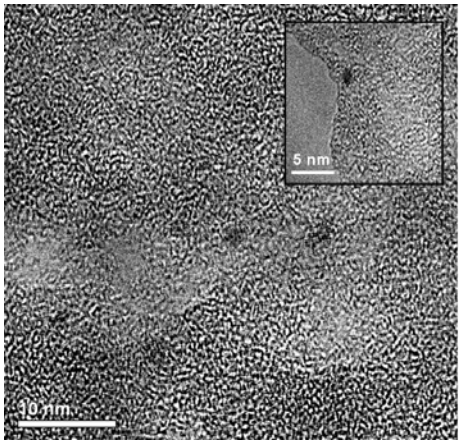

Fig.S2 The TEM images of BSA-Au nanoclusters

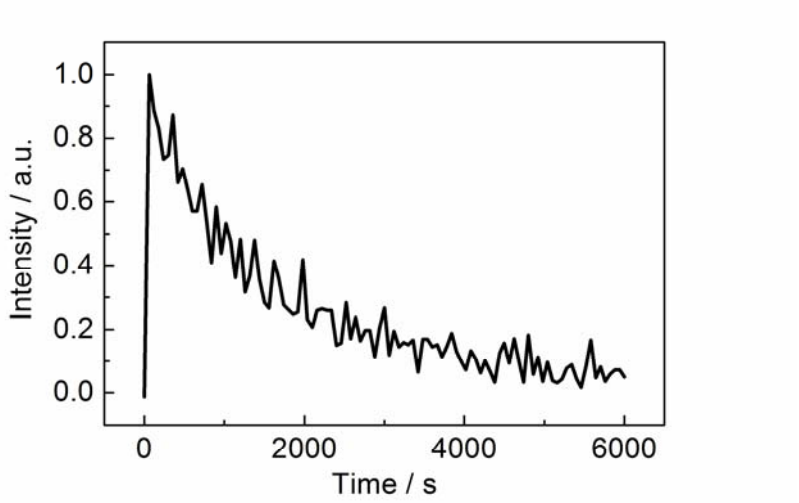

Fig.S3 Fluorescence decay of the BSA-Au nanoclusters as a function of time.

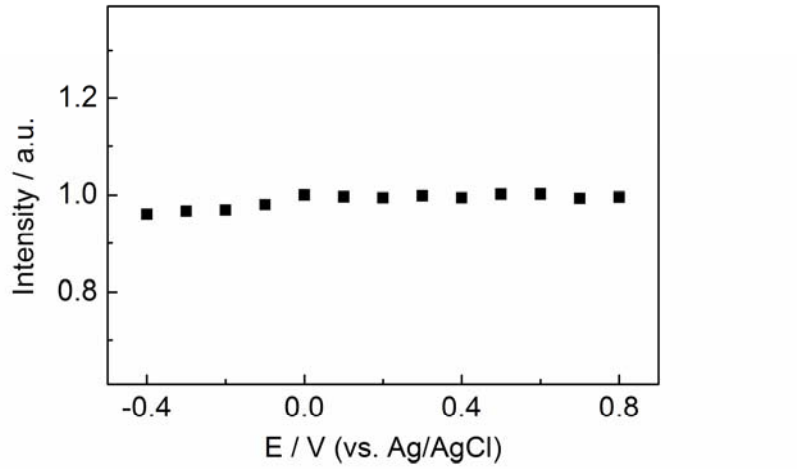

Fig.S4 The fluorescence stability of the Au nanoclusters-chitosan layer against the different applying potentials.

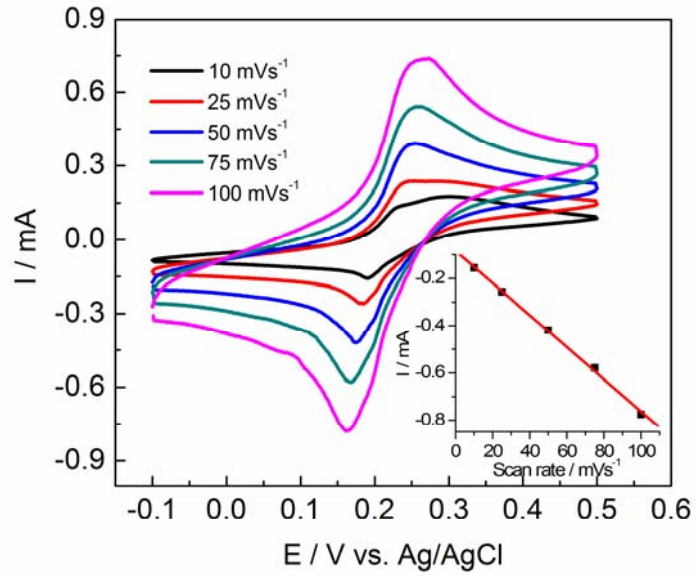

Fig.S5 Cyclic voltammograms at different scan rates (10, 25, 50, 75, 100 mV/s) of the prepared PB layer on the ITO electrode. Inset: Plots of reduction peak current versus the scan rate.

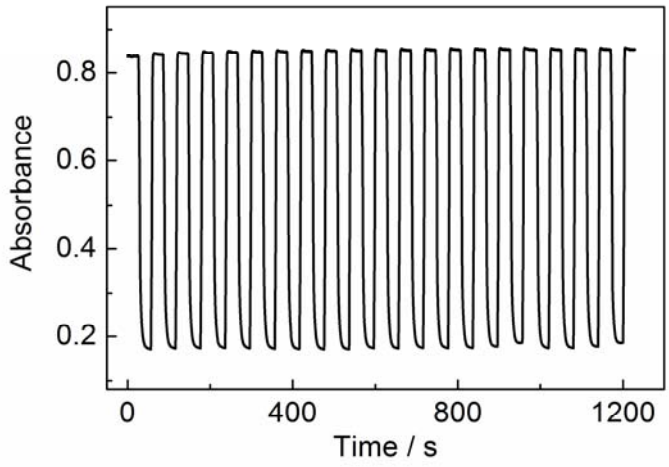

Fig.S6 The absorption response versus time during 20 consecutive switch cycles (0 V/0.5 V vs Ag/AgCl, 30s for each step) monitored at 697 nm.

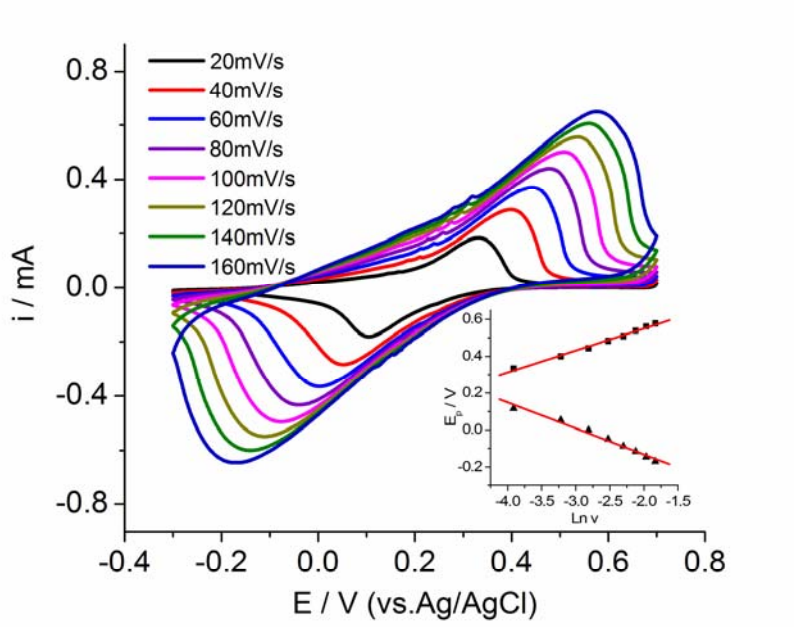

Fig.S7 Cyclic voltammograms at different scan rates (20, 40, 60, 80, 100, 120, 140, 160 mV/s) of the prepared multilayer structure on the ITO electrode. Inset: the fitted linear lines of the E_p versus Ln(v).

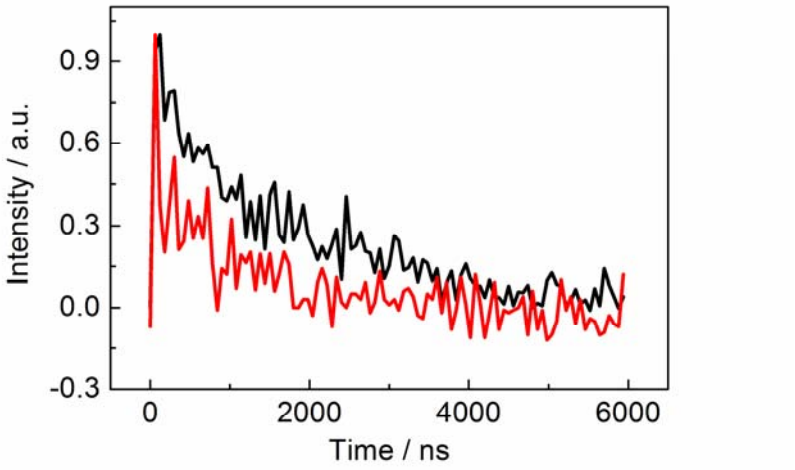

Fig.S8 Fluorescence decay of the hybrid film as a function of time. The black line represents the fluorescence decay at the potential of 0 V, while the red line is for the fluorescence decay after applying the potential of 0.5 V.

3. References

1. F. Montilla, I. Pastor, C. R. Mateo, E. Morallon, R. Mallavia, *J. Phys. Chem. B* 2006, **110**, 5914.
2. E. Laviron, *J. Electroanal. Chem.*, 1979, **100**, 263.
3. H. Z. Yu, Y. Q. Wang, J. Z. Cheng, J. W. Zhao, S. M. Cai, H. Inokuchi, A. Fujishima, Z. F. Liu, *Langmuir,* 1996, **12**, 2843.