

-Supporting Information-

Amplified Quenching of Electrochemiluminescence from CdS Sensitized TiO₂ Nanotubes by CdTe-Carbon Nanotube Composite for Detection of Prostate Protein Antigen in Serum

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1. Fabrication and characterization of CdS/TiO₂ electrode.

The CdS/TiO₂ NTs were synthesized according to the previous works,^{1,2} similarly to that described by Peng et al.³ Prior to anodization, a titanium ribbon (4cm×0.5cm) was ultrasonically cleaned in a dilute HF solution then water for 5 min each. The cleaned titanium ribbon with the area of 0.5 cm × 0.5 cm was immersed in an electrolyte containing 1.0 M NaF and 0.5% M (NH₄)₂SO₄ and anodized at 20 V with a platinum cathode (performed on the DC power supply) at room temperature for 3 hour. The un-anodized top part of the titanium ribbon was used as the electrical contact. After anodic oxidation, the samples were sonicated with ultrapure water, and dried in a N₂ stream. The resulting amorphous TiO₂ nanotubes were annealed at 500°C for 1 h with heating and cooling rates of 10°C/min in an O₂ atmosphere to crystallize the tube walls and improve their stoichiometry. CdS nanoparticles were deposited into the crystallized TiO₂ nanotubes by sequential chemical bath deposition (S-CBD) method. Typically, the sample was successively immersed in four different beakers for about 30 s in each beaker. One beaker contained 0.05 M Cd(NO₃)₂ aqueous solution, another contained 0.05 M Na₂S, and the other two contained ultrapure water to rinse the samples from the excess of each precursor solution. Such an immersion cycle was repeated for 10 times. After that, the samples became deep yellow. Finally, the samples were dried in a N₂ stream.

2. In-situ growth of CdTe NCs on MWNTs.

CdTe/MWNTs nanocomposites were synthesized using an in-situ growth method reported previously.^{4,5} The oxidized MWNTs suspension with different MWNTs amounts (0.010, 0.05, 0.10, 0.20, 0.30, 0.40 and 0.50 mg mL⁻¹) were mixed in CdCl₂ solution before adding freshly prepared NaHTe solution (5 μM). Sodium borohydride (NaBH₄) used to react with tellurium in water to produce sodium hydrogen telluride (NaHTe). Freshly prepared NaHTe solution was added to N₂-saturated CdCl₂ and MWNTs solutions at pH 10.0 in the presence of MPA as stabilizing agents.

The molar ratio of Cd^{2+} /stabilizer/ HTe^- was fixed at 1:2:0.5. The resulting mixtures were then subjected to reflux to control the in-situ growth of CdTe NPs on MWNTs at the temperature of 100 °C.

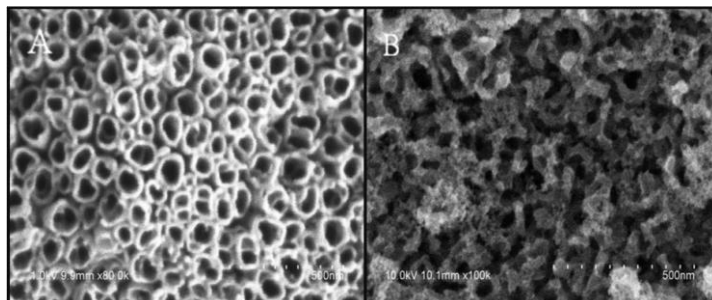


Figure.S 1. SEM images of A) TiO_2 NTs, B) CdS/TiO_2 NTs

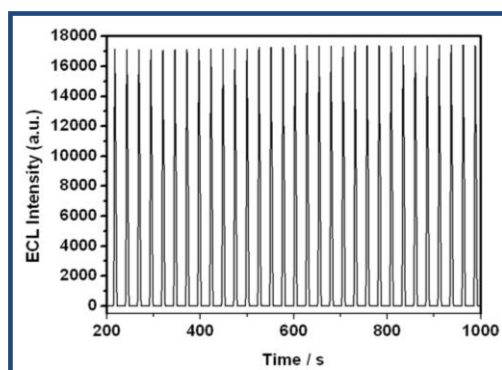


Figure S2 ECL emission from CdS/TiO_2 NTs electrode under continuous 20 cycles of cyclic scan. In 0.05M $\text{K}_2\text{S}_2\text{O}_8$ and 100 mM PBS (pH 8.3) with scan rate of 400 mV/s.

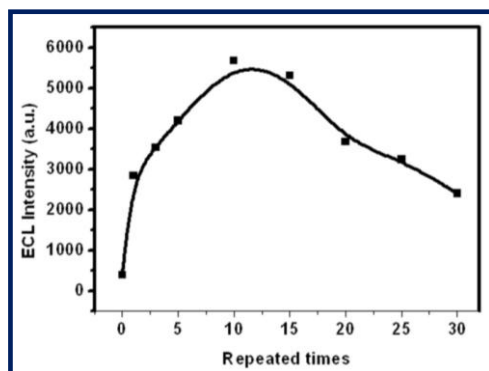


Figure S3. The dependence of ECL intensity of the $\text{CdS} / \text{TiO}_2$ NTs electrodes on the repeated time of the immersion cycle in 0.05 M $\text{Cd}(\text{NO}_3)_2$ and 0.05 M Na_2S aqueous solutions. In 0.10 M $\text{K}_2\text{S}_2\text{O}_8$, with pH of 8.3, Scan rate, 400 mV/s; voltage of PMT, 500 V;

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