Supplementary Information

Energy Transfer between CdS Quantum Dots and Au Nanoparticles in Photoelectrochemical Detection

Wei-Wei Zhao, Jing Wang, Jing-Juan Xu* and Hong-Yuan Chen
Key Laboratory of Analytical Chemistry for Life Science (Ministry of Education of China), School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China
* Corresponding author. Tel/Fax: +86-25-83597294; *E-mail address*: xujj@nju.edu.cn (J.J. Xu)

Experimental

1. Materials.

Indium tin oxide (ITO, type N-STN-S1-10 with ITO coating 180±20 nm, sheet resistance 8.1± 0.6 Ω cm^{-2}) is obtained from China Southern Glass Holding Co., LTD, Shenzhen, China.

Tris(2-carboxyethyl) phosphine hydrochloride(TCEP), PDDA (20%, w/w in water, molecular weight (200 000-350 000)), SiO_2 NPs (LUDOX SM-30, 30 wt %, average particle diameter c.a. 7 nm) and (3-aminopropyl)triethoxysilane (APTES) were obtained from Sigma-Aldrich. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) was purchased from Fluka. *N*-Hydroxysuccinimide **(**NHS), ascorbic acid (AA), thioglycolic acid (TGA) and monoethanolamine (MEA**)** were purchased from Sinopharm Chemical Reagent Co., LTD (Shanghai, China). $CdCl_2 \cdot 2.5H_2O$ was obtained from Shanghai Jinshan Tingxin Chemical Plant. $Na_2S \cdot 9H_2O$ was obtained from Shanghai Lingfeng Chemical Reagent Co., LTD (Shanghai, China). $HAuCl_4$ was purchased from Nanjing Chemical Reagent Co., LTD. Glutaraldehyde and $NaBH_4$ was purchased from Tianjin Chemical Reagent Institude. All other reagents were of analytical grade and were used as received. The washing buffer was 10 mM PBS (pH 7.4, M_{NaCl} = 0.3 M NaCl). All aqueous solutions were prepared using ultra-pure water (Milli-Q, Millipore). All the synthetic oligonucleotides were purchased from GeneTime Co., LTD (China) and the corresponding sequences were summarized in Table S1.

Table S1. The DNA Oligonucleotides Sequences

capture	5'-NH_2-$(CH_2)_6$-AGA TGC CGT GGT AGA TGC CGT GGT-3'
	5'-SH-$(CH_2)_6$-ACC ACG GCA TCT ACC ACG GCA TCT-3'
	(for the labeling with Au NPs)
target	
	5'-NH_2-$(CH_2)_6$-ACC ACG GCA TCT ACC ACG GCA TCT-3'
	(for the labeling with SiO_2 NPs)

2. Synthesis of CdS QDs

TGA-stabilized CdS QDs were synthesized by using a slightly modified procedure.[1] Briefly, 250 μL of TGA was added to 50 mL of 0.01 M $CdCl_2$ aqueous solution, N_2 was bubbled throughout the solution to remove O_2 for 30 min. During this period, 1.0 M NaOH was added to adjust the pH of the above solution to 11. After that, 5.5 mL of 0.1 M Na_2S aqueous solution was injected into this solution to obtain TGA-capped water-soluble CdS QDs and the reaction mixture was refluxed under N_2 atmosphere for 4 h. Finally, the desired TGA-stabilized CdS QDs were obtained and then diluted with the same volume of water and stored in a refrigerator at 4℃ for further use.

3. Fabrication of CdS modified electrodes

The ITO slices were cleaned by immersion in 2M boiling KOH solution dissolved in 2-propanol for 15 min, followed by washing copiously with water and dried at 120 ℃. The CdS modified ITO electrode was synthesized by alternately immersing the cleaned ITO slices into a solution of 2% PDDA containing 0.5 M NaCl and the CdS QDs solution for 10 min, and this process was repeated for three times. The electrodes were carefully washed with doubly distilled water after each dipping step.

4. The Immobilization of Capture DNA

Immobilization of capture DNA to the CdS QDs modified electrodes was accomplished via the commonly used EDC coupling reactions between COOH groups on the surface of CdS QDs and the NH_2 groups of capture DNA. The CdS QDs modified electrodes were immersed in a solution containing 10 mM EDC and 20 mM NHS for 50 min at room temperature. After rinsing, 20 μL of 1 μM capture DNA was dropped onto the surface of the electrode and incubated at 4℃ overnight. The as-prepared DNA biosensor was washed thoroughly to remove the unlinked capture DNA before the blocking with 1mM MEA at 4℃ for 2 h and final rinsing.

5. Synthesis of Au NPs

Au NPs with average diameter 5 ± 1 nm were prepared through the reduction of $HAuCl_4$ by sodium $NaBH_4$ according to the reported methods with slight modifications. Briefly, 0.6 mL of 0.1 M ice cold $NaBH_4$ was added to 20 mL of aqueous solution containing 2.5×10^{-4} M $HAuCl_4$ under stirring, and the solution immediately turned to an orange-red color, indicating the formation of Au NPs. Then the solution was kept under stirring in the ice bath for 10 min and for another 3 h at room temperature with the color changing from orange-red to wine red. The nearly monodispersed Au NPs had an average diameter of 5 ± 1 nm as characterized by TEM and thus the final concentration of the Au colloid solution was estimated to be 6×10^{-8} M. The prepared Au NPs were kept in a refrigerator at 4 ºC for further use.

6. Preparation of Au NPs-labeled target DNA

Au NPs-target DNA oligonucleotide bioconjugates was synthesized by derivatizing of the prepared Au NPs colloid with 5'-thiol-capped target DNA oligonucleotides. The 5'-thiol-capped DNA was activated with TCEP before use in order to reduce disulfide bonds. In typical experiments, 5 μL of 50 μM capture DNA probe was added into 245 μL prepared Au NPs solution containing 0.1M NaCl. After shaking gently for 24 h at room temperature, the conjunction was isolated by centrifugation for 30 min at 15 000 rpm. After removal of the supernatant, the precipitate was washed, recentrifuged, and redispersed in 10 mM PBS (pH 7.4, M_{NaCl}

= 0.1 M). The Au NPs-labeled DNA targets solution was stored at 4℃. Different concentrations of Au NPs-labeled DNA targets were prepared by diluting the obtained Au NPs-labeled DNA targets solution with 10 mM PBS (pH 7.4, M_{NaCl} = 0.1 M) solution prior to the hybridization assay. For comparison, 6 $\times 10^{-8}$ M SiO_2 NPs of similar size were employed for the labeling of oligonucleotide DNA targets according to the literature.[2] Briefly, the NH_2 groups functionalized SiO_2 NPs were synthesized via surface modification of SiO_2 NPs by APTES. Then the NH_2-modified target DNA was connected with the NH_2 groups on the surface of the SiO_2 NPs by glutaraldehyde to obtain the SiO_2 NPs-target DNA oligonucleotide bioconjugates.

7. Hybridization Procedures

The hybridization reaction was carried out by dropping 20 μL of solution of NPs-labeled target DNA containing different concentration of oligonucleotide on the capture DNA immobilized ITO electrode for 1h incubation at 37℃ in the presence of 20 mM $MgCl_2$. After that, the electrode was washed thoroughly to remove the unhybridized DNA targets followed by the PEC measurement.

8. Instrumental

Photoelectrochemical measurements were performed with a homemade photoelectrochemical system. A 500W Xe lamp equipped with monochromator was used as the irradiation source. Photocurrent was measured on a CHI 750a electrochemical working station using a Pt wire as the counter electrode, a saturated Ag/AgCl as the reference electrode and a modified ITO electrode with an area of 0.25 cm^2 as the working electrode. All the photocurrent measurements were performed at a constant potential of 0 V (vs saturated Ag/AgCl). A 0.1 M PBS (pH 7.4, M_{NaCl} = 0.1 M) containing 0.08 M AA was used as the supporting electrolyte for photocurrent measurements. The solutions were deaerated by bubbling highly pure nitrogen for at least 15 min before experiment and a nitrogen atmosphere was kept over the test solution during the photoelectrochemical detections. UV-vis absorption spectra were obtained on a Shimadzu UV-3600 UV/vis spectrophotometer (Shimadzu Corporation,

Japan). Transmission electron microscope (TEM) were performed with a JEOL model 2000 instrument operating at 200 kV accelerating voltage. UV–vis absorption spectra were acquired with a Shimadzu UV-3600 UV/vis spectrophotometer. Photoluminescence (PL) spectra were obtained on a RF-540 spectrophotometer (Shimadzu Co)

Discussion about the photocurrent reduction mechanism.

The transfer of the photoexcited electrons of CdS QDs to the gold could happen but on the stipulation that the two particles are in close contact, under which condition that the electron transfer would result in enhanced photocurrent.[3] However, when the two particles are in large distance, the interparticle electron transfer could not happen.

In order to illustrate that the photocurrent reduction in the mauscript is do from energy transfer and the inhibited electron transfer process between CdS QDs and the donor (ascorbic acid), not the transfer of the photoexcited electrons to the gold, we do the following experiment: The 5 ± 1 nm citrate-capped Au-NPs (negatively charged)[4] was equipped to the CdS QDs modified ITO electrode via the connection of positively charged PDDA to bring the two particles in close contact, as shown in the following Figure S1a. The subsequent PEC measurements of the hybrid Au NPs/CdS QDs electrode displayed that an slightly increase ca. 7% of photocurrent intensity as compared to the initial value of bare CdS QDs modified electrode, whereas the sharp photocurrent reduction of about 64% via 24 bases DNA linking (Figure S1b) has been observed in the manuscript.

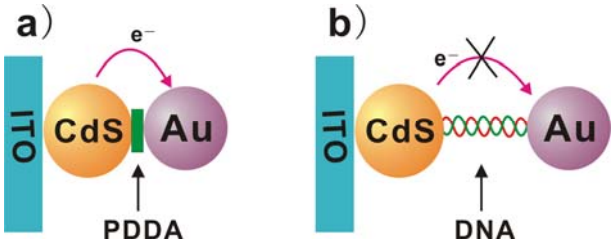

Figure S1. Assembly of Au NPs/CdS QDs hybrid system via (a) electrostatic adsorption and (b) duplex DNA linking.

A comparison of enhanced photocurrent intensity of Figure S1a with Figure S1b could clarify the problem. Here, in the case of Figure S1a, electrons from photoexcited electron-hole pairs in CdS QDs can tunnel and be captured in Au NPs followed by nonradiative recombination with remaining holes at the QD-Au interface, or transferred by Au NPs acting as electron carriers to the bulk electrode surface. The capture of the electrons in the Au NPs separate the e-h pairs in the CdS QDs, hence retarding the e-h recombination and improving the photocurrent generation efficiency.

Under the circumstance of Figure S1b of larger interpatricle distance, if the electron transfer from CdS QDs to Au NPs is still be present whilst in the hypothetical case of absence of energy transfer, we expect in such systems the slightly enhanced photocurrent. On the contrary, a prominent photocurrent reduction was observed, demonstrating the absence of the interparticle electron transfer from the CdS QDs to Au NPs. In fact, the increase in potential barrier between QDs and Au NPs with the larger interparticle distance will drastically diminish the probability of photoelectron tunneling into gold.[5] In the present case, the interparticle distance is controlled as long as ~ 8 nm (the length of 3 base pairs is considered as 1 nm generally) that it is impossible for the happening of interparticle electron transfer from CdS QDs to Au NPs.

Obviously, energy transfer is not the only mechanism responsible for photocurrent signaling, especially for QDs in close contact with Au NPs. From the experimental results, we may conclude that the prompt interparticle electron transfer between CdS QDs and Au NPs, which is mainly responsible for the enhanced photocurrent intensity, is very efficient when the two particles are in close contact and can completely compensate the quenching effect of energy effect. However, in the case of Figure S1b in which it is impossible for the occurrence of interparticle electron transfer, the mechanism of sharp photocurrent reduction should be attributed to energy transfer.

References.

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