Supporting Information

Size-Dependent Energy Transfer between CdSe/ZnS Quantum Dots and Gold Nanoparticles

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Experimental Section

Materials. Cadmium oxide (CdO, 99.99+%), zinc oxide (ZnO, 99.99%), sulfur (powder, 99.98%), trioctylphosphine oxide (TOPO, tech. 90%), 1-octadecene (ODE, tech. 90%), oleic acid (tech. 90%), octyldecylamine (ODA, tech. 90%), trioctylphosphine (TOP, tech. 90%), selenium (powder, 99+%), . *p*-mercaptobenzoic acid (MBA, Technical grade 90%), 3-mercaptopropionic acid (MPA, 99+%), $Hg(NO_3)_2$ and 5 M NaCl stock solution were purchased from Sigma-Aldrich. *n*-tetradecylphosphonic acid (TDPA) was purchased from PCI Synthesis. Methylene dichloride (CH_2Cl_2, HPLC grade), methanol (ACS grade) and acetone (ACS grade) were purchased from Fisher Scientific. Chloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$), $NaBH_4$ (98%) and ethylenediamine (99%) were obtained from Alfa-Aesar. 80 nm sized gold nanoparticles (NPs) were purchased from BioAssay Works Naked Gold (USA). D.I. water was obtained from a Milli-Q academic Millipore system. All chemicals and solvents were obtained from the commercial sources and used directly without any further purification, and all glassware were cleaned successively with HNO_3 and D.I. water, and then dried before use.

Synthesis of CdSe/ZnS QDs. CdSe/ZnS QDs were synthesized by the well-established method with slight modification.[1,2] CdO (0.4 mmol), TDPA (0.2 g), ODA (1.0 g) and TOPO (2.5 g) were added into a 50 mL three-neck flask and were evacuated for 30 min at 100 ^{o}C. The mixture was then heated to 300-320 ^{o}C under Ar-flow to obtain a colorless clear solution. After that, the temperature was lowered to 260-270 ^{o}C for the injection of TOPSe (0.03 g Se in 2.4 mL TOP). Following this, the temperature was lowered to 240 ^{o}C for CdSe growth and the fluorescence emission was monitored using the 365 nm UV light. Once the desired fluorescence emission was observed, the

temperature was lowered to about 220 ^{o}C, and the calculated amount of the Zn- or S-stock solution (0.407 g ZnO in 20 mL oleic acid and 30 mL ODE for 0.1 M Zn-stock solution, and 0.16 g S in 50 mL ODE for 0.1 M S-stock solution) for each ZnS monolayer was alternately injected. The CdSe/ZnS QDs with 2 ZnS monolayers, 3.4 nm in diameter and yellow fluorescence emission around 570 nm were obtained.

Surface Modificantion of CdSe/ZnS QDs with MPA. The as-made QDs were coated by the hydrophobic ligand TOPO and ODA, and thus the as-made QDs cannot dissolve in the aqueous solution. The water soluble MPA-QDs were prepared through the ligand exchange method. Firstly, the MPA-KOH methanolic stock solution was obtained by adding 4 mL MPA and 3.0 g KOH into 40 mL methanol. 5 mL TOPO-coated QDs in CH_2Cl_2 with the optical density (O.D.) of 1.9 were precipitated and purified 4 times by addition of methanol and acetone, and redispersed in 1 mL CH_2Cl_2, followed by the centrifugation at a speed of 3,000 *rpm* to remove impurities. 200 μL of MPA-KOH methanolic stock solution was added and incubated overnight. The precipitates can be observed, indicating the formation of the hydrophilic QDs. The suspension was centrifuged at a speed of 3,000 *rpm* and washed 4 times by CH_2Cl_2 and methanol to remove the excess MPA and exchanged organic ligands. The resulting precipitates were dispersed into 20 mL 0.3 M PBS (0.3 M NaCl, 10 mM NaH_2PO_4/Na_2HPO_4 buffer solution with pH=7), and then centrifuged at a very low speed to obtain a clear water soluble MPA-QDs for further use.

Synthesis of Oligonucleotide-Functionalized CdSe/ZnS QDs and Gold Nanoparticles. Gold nanoparticles with different sizes were synthesized through the reduction of $HAuCl_4 \cdot 3H_2O$ by $NaBH_4$ or trisodium citrate.[3-5]

(1) *Synthesis of 15 nm sized gold nanoparticles*. Typically, 1 mL chloroauric acid trihydrate (20 mM) aqueous solution was added to 50 mL D.I. water, and then was heated to boiling under magnetic stirring. The wine-red solution can be obtained after 30 min boiling, and then naturally cooled to room temperature. As a result, 15 nm gold nanoparticles are obtained.

(2) *Synthesis of 3 nm sized gold nanoparticles*. In a typical process for synthesis of 3 nm gold nanoparticles, 0.5 mmol (0.197 g) of $HAuCl_4 \bullet 3H_2O$ dissolved as a 5% (w/v) aqueous solution will be mixed with 1.5 mmol of MBA in 100 mL methanol to give a transparent solution in a 250 mL flask, and then 15 mL NaOH aqueous solution (0.3 M) will be added. Then, a freshly prepared 25 mL aqueous sodium borohydride ($NaBH_4$) solution (0.2 M) will be added at a rate of 5 mL per min under vigorous stirring. After further stirring for 1 hour, the solvent will be removed after centrifuging at 10,000 *rpm* for 5 min. Then the precipitate will be washed twice with a 20% (v/v) water/methanol solution through an ultrasonic redispersion-centrifugation process to remove the inorganic or organic impurities. This process will be repeated with 99.8% methanol to remove unbound thiol. Finally, the precipitate will be suspended in ethanol and dried in air.

(3) 80 *nm sized gold nanoparticles.* The 80 nm sized gold nanoparticles were purchased from a commercial source (BioAssay Works Naked Gold, USA).

(4) *Preparation of DNA-functionalized QDs and gold nanoparticles*. The ssDNAs were synthesized, purified and deprotected according to the well-documented protocol.[6] Functionalization of QDs and gold nanoparticles with DNA was carried out according to the well-established procedures by Mirkin[7] and Nie groups[8]. The water-soluble QDs and

gold nanoparticles were attached by synthetic ssDNA with a C_6 spacer appended to the 5'-phosphate backbone terminus of a 10 bp (base pair), 20 bp and 30 bp. The amount of the loading DNA was controlled to at most 1 ssDNA molecule per particle, based on the UV-vis absorption spectra. The spectra of the solution before and after conjugation were recorded, and the loading of ssDNA per particle was calculated from the absorbance difference at 260 nm based on 1 O.D. (260 nm)=50 ng DNA/μL. Also, the particle concentration was obtained from the UV-vis absorption spectrum using the molar extinction coefficient at the wavelength of maximum absorption ($\varepsilon_{(QDs,\ 570\ nm)}$=$2.0\times10^5$ $M^{-1}\cdot cm^{-1}$,[9] $\varepsilon_{(3\ nm\ Au,\ 506\ nm)}$=$1.1\times10^5$ $M^{-1}\cdot cm^{-1}$,[10] $\varepsilon_{(15\ nm\ Au,\ 520\ nm)}$=$1.0\times10^8$ $M^{-1}\cdot cm^{-1}$,[11] and $\varepsilon_{(80\ nm\ Au,\ 550\ nm)}$=$6.9\times10^{10}$ $M^{-1}\cdot cm^{-1}$ [12]).

Gold Nanoparticle-QD Conjugates. Gold nanoparticle-QD conjugate ensemble was prepared by the formation of thymidine-Hg^{2+}-thymidine (T-Hg^{2+}-T) complexes in the presence of Hg^{2+}, First, the assay solution was made by adding DNA-gold conjugates (6.0 nM) and DNA-QD conjugates (6.0 nM) into the 0.3 M PBS solution containing 0.3 M NaCl, 10 mM Na_2HPO_4/NaH_2PO_4 and 0.1 mM ethylenediamine. Following this, the quenching assay was carried out by adding various concentrations of Hg^{2+} into the assay solution. The fluorescence intensity at 570 nm was monitored.

Characterization. The size and morphology of the nanoparticles were observed with a JEM 2100F transmission electron microscope (TEM) with an acceleration voltage of 200 kV. UV-visible absorption spectra were measured in the range of 200-800 nm with a Shimadzu UV-2550 spectrometer. The fluorescence (FL) emission spectra were measured using a Hitachi F-7000 fluorescence spectrophotometer. The FL quantum yield (QY) was determined using Rhodamine 6G as a reference.

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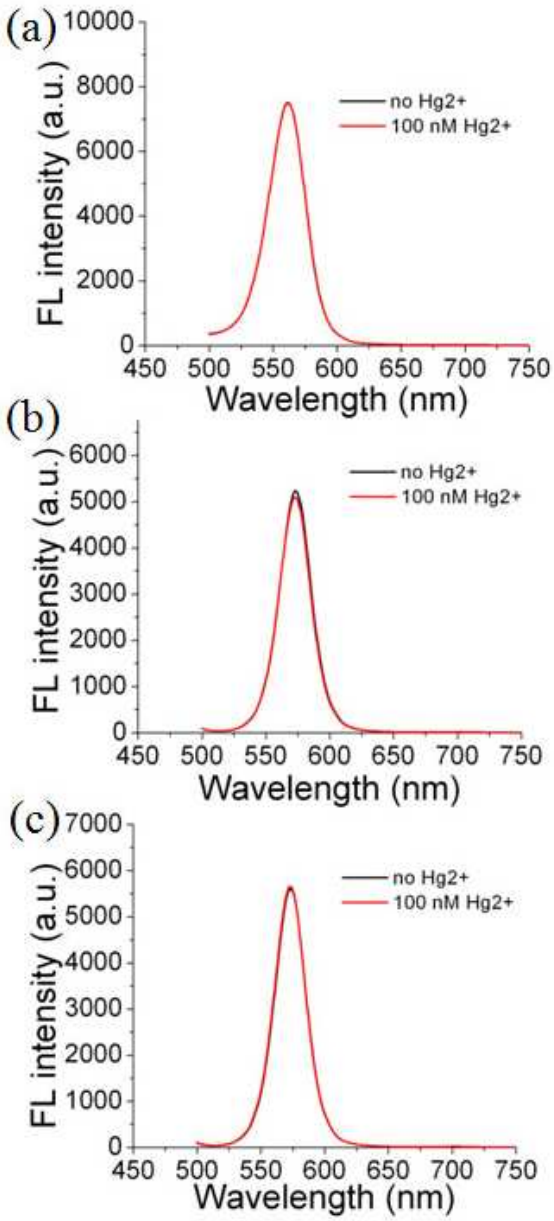

Figure S1. Fluorescence spectra of the solution with (a) 10 base DNA-, (b) 20 base DNA- and (c) 30 base DNA-functionalized QDs without gold nanoparticles in the absence and presence of 100 nM Hg^{2+}. The FL intensity shows no observable change after addition of 100 nM Hg^{2+}, indicating that Hg^{2+} makes negligible contribution to fluorescence quenching of the QDs.

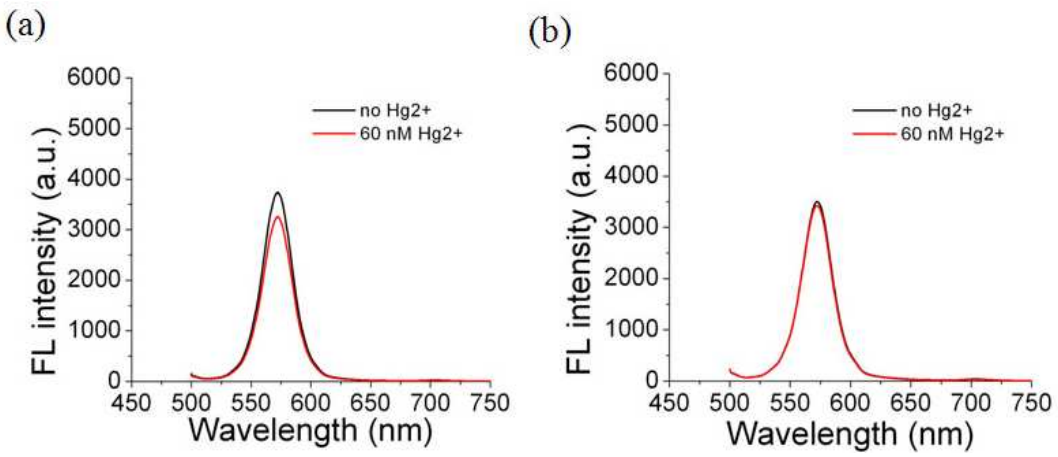

Figure S2. Fluorescence emission spectra of the solution containing the quantum dots and the 3 nm sized gold nanoparticles functionalized by DNA of (a) 20 base pairs and (b) 30 base pairs in the absence and presence of 60 nM Hg^{2+}, respectively.

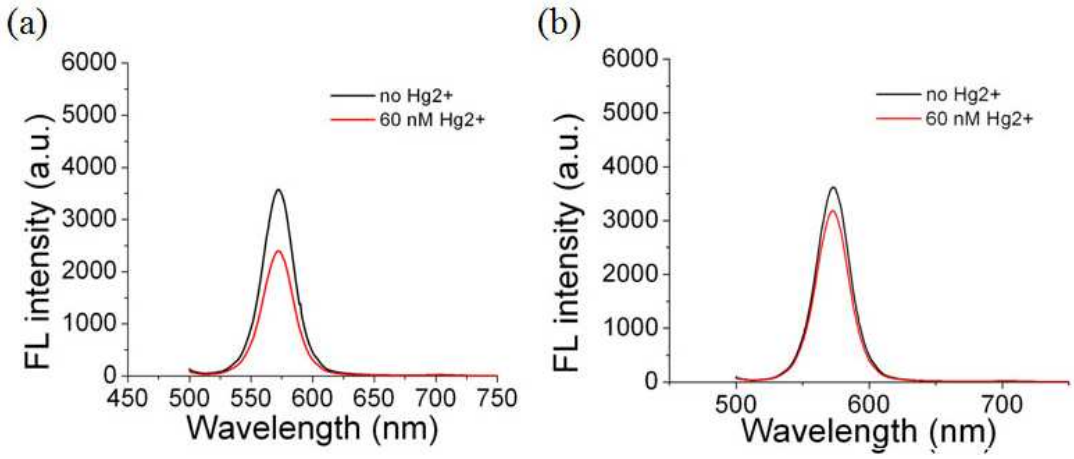

Figure S3. Fluorescence emission spectra of the solution containing the quantum dots and the 15 nm sized gold nanoparticles functionalized by DNA of (a) 20 base pairs and (b) 30 base pairs in the absence and presence of 60 nM Hg^{2+}, respectively.

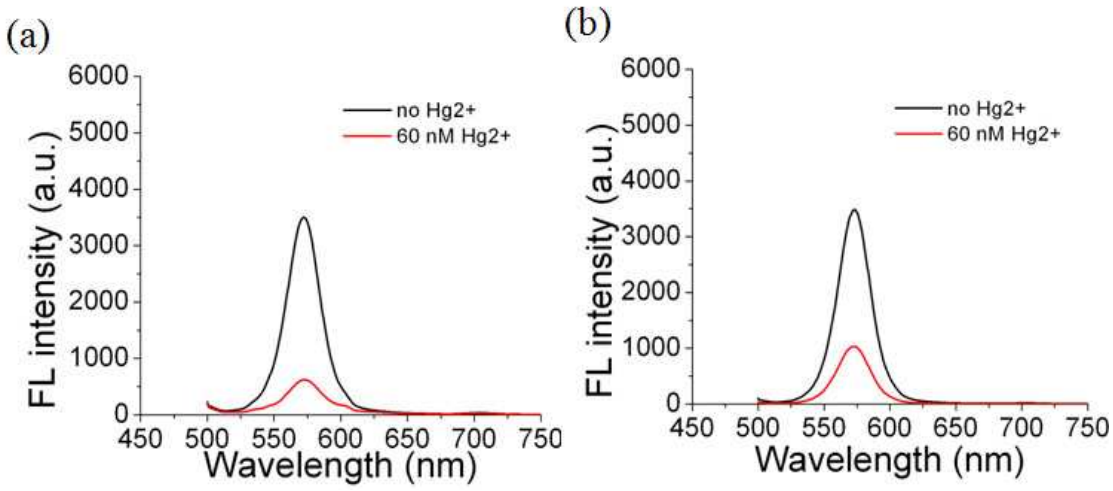

Figure S4. Fluorescence emission spectra of the solution containing the quantum dots and the 80 nm sized gold nanoparticles functionalized by DNA of (a) 20 base pairs and (b) 30 base pairs in the absence and presence of 60 nM Hg^{2+}, respectively.