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Electronic Supplementary Information

Au/SiO_2 Core/Shell Nanoparticles Enhancing Fluorescence Resonance Energy Transfer Efficiency in Solution

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Synthetic Procedures:

Chemicals.

$HAuCl_4$ (99.99%) and 3-aminopropyltriethoxysilane (APTES, 99.99%) were purchased from Aldrich. Tetraethyl orthosilicate (TEOS, 98%) was purchased from Fluka. Sodium citrate (A.R.) was obtained from Beijing Chemical Plant. R-phycoerythrin (RPE) was purchased from H & R Bioscience Co., Ltd.. All the chemicals were used without further purification. Deionized water was purified through a Milli-Q water purification system and the resistivity was 18.2 MΩ·cm.

Synthesis of gold core nanocrystals

Au core nanocrystals (NCs) were prepared according to the standard sodium citrate reduction method. Typically, 45 mL deionized water and 5 mL $HAuCl_4$ (2.5 mM) aqueous solutions were mixed in a three-neck flask and heated to 100 °C. Subsequently, 8 mL of 1% sodium citrate solution was quickly added into the flask. The color of the solution rapidly changed from tint yellow to black and deep purple. After one hour, the Au nanocrystals were cooled to room temperature and kept ready for the next silica encapsulation. As is shown in the FESEM of Fig. S3a, the size of as-prepared Au core was mainly 20 nm.

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Synthesis of Au/SiO_2 core/shell nanoparticles

Au/SiO_2 core/shell nanoparticles (NPs) were synthesized according to a modified procedure from ref. 1. Firstly, 5 mL Au core stock solutions were diluted to 50 mL with non-aqueous alcohol. Without any surface activation procedure, 0.5 mL TEOS and 0.25 mL ammonia solution were added to the gold core solution. The Au/SiO_2 core/shell nanoparticles (shell thickness ~ 80 nm) were successfully prepared after 3 hours stirring. Finally, 20 μL APTES was added to 10 mL of pre-synthesized Au/SiO_2 core/shell NPs to functionalize the silica surface with positively charged amino groups. The concentration of the resulted Au/SiO_2 core/shell NPs was calculated to be about 60 nM used for the next titration experiments.

Synthesis of aqueous CdTe/CdS core/shell quantum dots and formation of Au/SiO_2/QDs nanocomposites

The 3-mercaptopropionic acid stabilized CdTe/CdS core/shell QDs were synthesized according to our previous work.[2] The negatively charged CdTe/CdS QDs were electrostatically adsorbed onto the surface of the Au/SiO_2 core/shell nanoparticles (NPs) self-assembly to form Au/SiO_2/QDs nanocomposites via simple titration of aqueous QDs solution with the prefabricated Au/SiO_2 NPs and a gentle stirring afterwards.

Characterization:

The size and morphology of Au core NCs, Au/SiO_2 core/shell nanoparticles and Au/SiO_2/QDs nanocomposites were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800). Ultraviolet-visible (UV-vis) absorption and fluorescent emission spectra were measured at room temperature by a UV-3101 spectrophotometer and a Hitachi F-4500 fluorescence spectrofluorimeter, respectively. Fluorescent lifetimes were measured using a time-correlated single photon counting technique using the FL920-fluorescence lifetime spectrometer (Edinburgh instrument). The recorded decay curves were fitted with a bi-exponential function which was de-convoluted with the system response.

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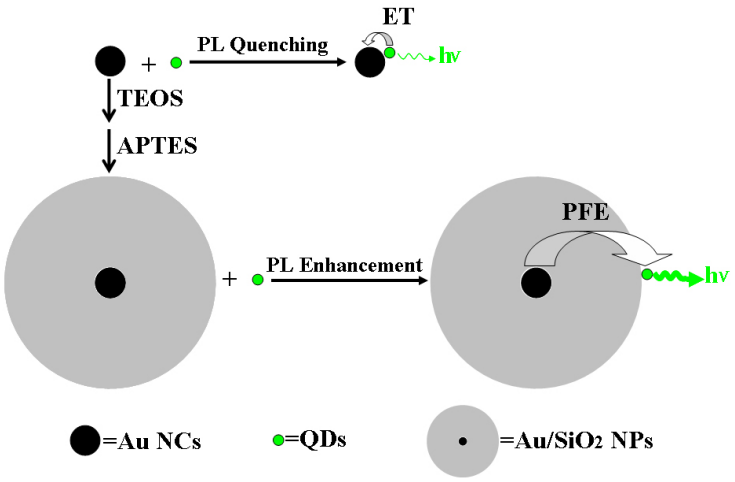

Scheme S1 Schematic depiction of the ET process from CdTe/CdS QDs to Au NCs and the plasmonic field enhanced effect of Au/SiO_2 NPs onto CdTe/CdS QDs.

There have been some studies on the distance related enhancement effect by, for example, the group of Klimov. As we have stated, absorption and scattering of Au NPs affect contradictorily the emission of a chromophore in the vicinity, and the distance is more critic for the absorption function. Therefore in order to feature the emission enhancement the distance should be long to such an extent that the absorption, and thus the quenching, is minimized while the scattering is not significantly affected. This was the motivation of coating 80 nm SiO_2 shell thickness in our case.

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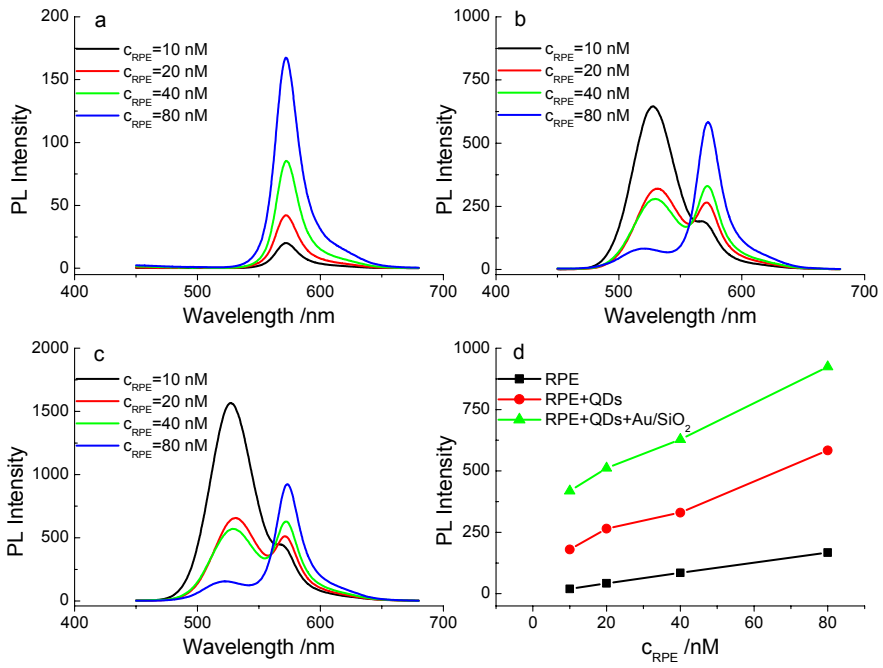

Fig. S1 PL spectra of the RPE solution (a), RPE plus QDs solution (b), RPE plus Au/SiO_2/QDs nanocomposites solution (c), and the relationship between the concentration of RPE and the PL intensity at the RPE emission wavelength (d). The concentration of RPE (a,b,c) was increased from 10 to 20, 40, and 80 nM, and the concentration of the QDs (b,c) and Au/SiO_2 (c) were kept constant.

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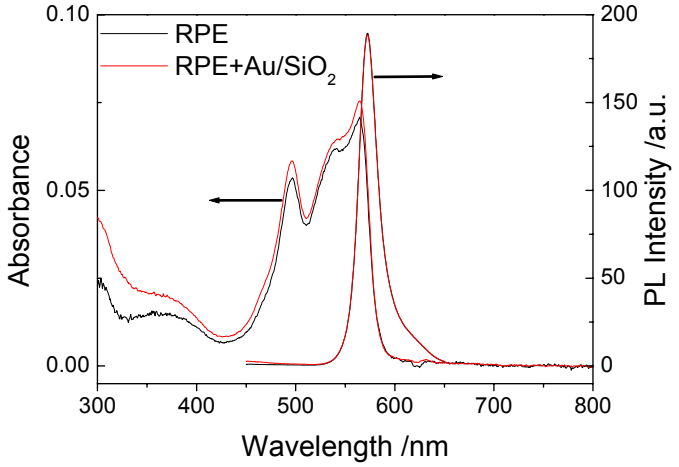

Fig. S2 Absorption and fluorescent spectra of the RPE molecules with and without the presence of the Au/SiO_2 NPs.

According to our understanding the silence of Au/SiO_2 NPs to enhance the fluorescence of RPE can be related with the nature of the enhancement mechanism. Recently it was reported that the more the emission of a chromophore overlaps with the scattering of the plasma in spectrum, the more the enhancement will be.[3] Based on these results we should not expect a significant enhancement of RPE emission in RPE-Au/SiO_2 solution because here the fluorescent spectrum of RPE is centered at 575 nm, whereas the plasma absorption peak is located around 523 nm.

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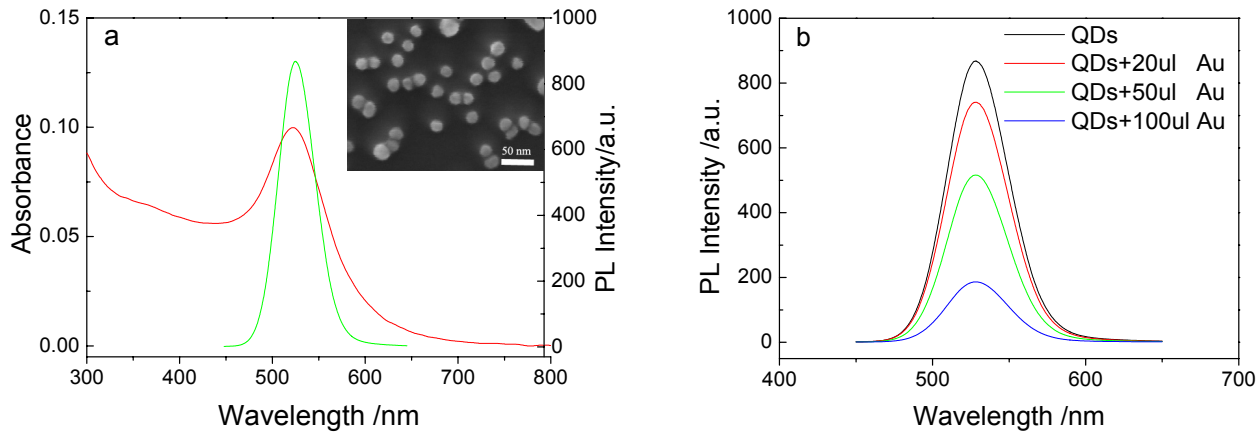

Fig. S3 (a) Absorption spectrum (red line) of Au NPs and PL spectrum (green line) of CdTe/CdS QDs. Inset shows the FE-SEM image of the gold NPs, the scale bar is 50 nm. (b) PL spectra of CdTe/CdS QDs with different volumes of Au solutions. The excitation wavelength was 350 nm.

The gold NCs, prepared using sodium citrate as a reagent to reduce the tetrachloroauric acid in aqueous solutions, were spherical with diameter of 20±3 nm (see inset of Fig. S3a). The plasmon resonance absorption was observed peaking at 523 nm (see Fig. S3a). The emission of the CdTe/CdS QDs (λ_{em}=528 nm) are expected to be quenched by the gold NCs, which is due to the energy transfer (ET) or charge transfer (CT) process.[4-7] Here, the gold NPs were treated with CTAB to own the amino groups on the surface, and then combined with the carboxylic QDs to verify the ET/CT process. As shown in Fig. S3b, when we drop the Au NCs into the CdTe/CdS QDs solutions, the PL intensity of the QDs is decreased due to the ET or CT between the chromophore and the metal NCs. As the volume of the Au NCs increases, the PL intensity drops gradually. Thus, the PL quenching efficiency increases steadily as the amount of Au NCs increases.

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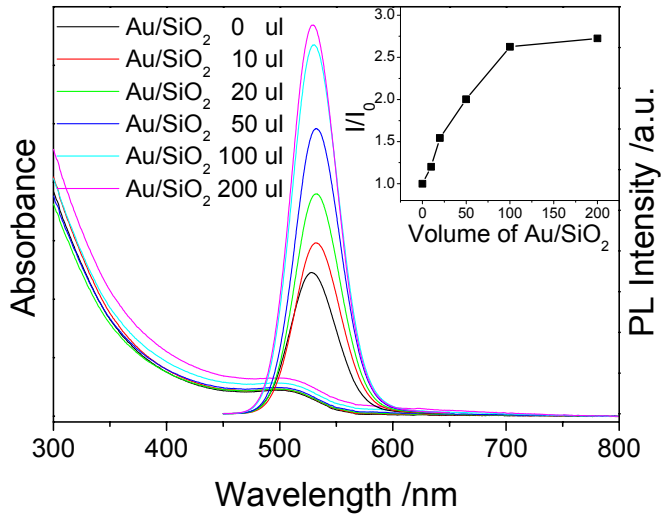

Fig. S4 Absorption and PL spectra of CdTe/CdS QDs with different volumes of Au/SiO_2 NPs. Inset is the variation of the PL intensity. The excitation wavelength was 350 nm.

As shown in Fig. S4, when the positive Au/SiO_2 NPs were dropped into the QDs solution, the absorption intensity was increased with increasing the concentration of Au/SiO_2 NPs due to the additional absorption of the Au/SiO_2 NPs. At the same time, the PL intensity was almost linearly increased until the Au/SiO_2 NPs was saturated with 100 μL. When the amount of Au/SiO_2 NPs was 100 μL, the increased value reached 2.6 folds. The primary red-shift of the PL peak of the CdTe/CdS QDs was due to aggregation of the CdTe/CdS QDs onto the surface of the Au/SiO_2 NPs.[8] With the increase volume of Au/SiO_2 NPs in the aqueous solution, more and more CdTe/CdS QDs can be symmetrically adsorbed onto the surface of Au/SiO_2 NPs, as a result, the aggregation phenomenon is gradually restricted and the PL spectra shift to blue side concordantly.

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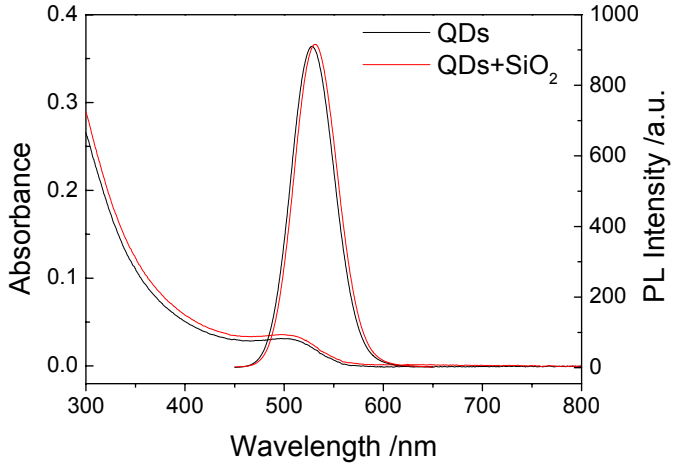

Fig. S5 PL spectra of CdTe/CdS QDs with and without the presence of 180 nm SiO_2 NPs. The excitation wavelength was 350 nm.

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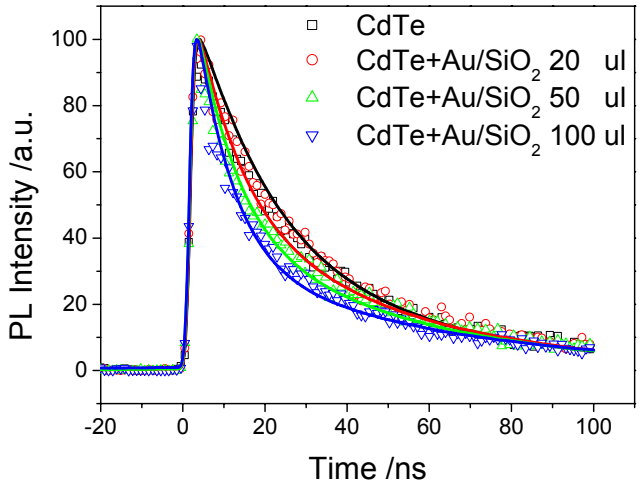

Fig. S6 Fluorescent decay curves and the fitted curves of CdTe/CdS QDs with addition of different volume of Au/SiO_2 NPs. The excitation wavelength was 350 nm.

Au/SiO_2 (μL)	τ_1 (ns)	B_1%	τ_2 (ns)	B_2%	k_r (s^{-1})	QY (%)
0	16.4	30.8	44.0	69.2	0.84×10^7	30
20	14.0	31.4	42.6	68.6	1.38×10^7	46
50	9.5	31.4	41.7	68.6	1.90×10^7	60
100	8.7	33.2	40.0	66.8	2.66×10^7	79

Table S1. The fast lifetime (τ_1), slow lifetime (τ_2), components B_1% and B_2% of τ_1 and τ_2, radiative rate (k_r), and QY of the relative samples shown in Fig. S6.

The decay traces can be well fitted with a bi-exponential model $I(t)=B_1exp(-t/\tau_1)+B_2exp(-t/\tau_2)$, where τ_1 and τ_2 represent the time constants, and B_1 and B_2 are the corresponding amplitudes, respectively. The average lifetime τ was calculated by $\tau=(B_1\tau_1^2+B_2\tau_2^2)/(B_1\tau_1+B_2\tau_2)$, and the radiative rate of the QDs was estimated using the relations, $QY=k_r/(k_r+k_{nr})$ and $1/\tau= k_r+k_{nr}$. The fast lifetime (τ_1), slow lifetime (τ_2), components B_1% and B_2% of τ_1 and τ_2, radiative rate (k_r), and QY are summarized in Table S1. Non-exponential luminescence decay of QDs is widely observed. But its origin is still under debate. In our case bi-exponential function is sufficient to describe the time trace. According to our observation, the

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two pre-exponential factors B_1 and B_2 do not change when Au/SiO_2/QDs ratio varies; unlike the behavior of τ_1 and τ_2. This phenomenon assures that both the long- and short-lived components come from a same particle, otherwise one would expect a Au/SiO_2/QDs ratio-dependent B_1/B_2. With the strengthening of PFE effect by adding more Au/SiO_2 NPs in the QDs solution, the fast lifetime gradually decreases from 16.4 to 8.7 ns, and the radiative rate is increased from 0.84×10^7 to 2.66×10^7 S^{-1}. Theoretically luminescence QY of QDs (Q_D) is related with the efficiency of FRET (Φ_{FRET}) from QDs to RPE following the equations (equation 2 and 3).[9]

$$\Phi_{FRET}=1/[1+(R/R_0)^6] \quad (2)$$

$$R_0^6=9000(\ln10)\kappa^2Q_DJ/128\pi^5N_An^4 \quad (3)$$

Taking the parameters, such as FRET efficiency in the absence of the Au/SiO_2 NPs is 37% and other relevant parameters from Table S1, the FRET efficiency, in the presence of the Au/SiO_2 NPs, can be deduced from the above equations as 61%, which is very close to 69% obtained from Φ_{FRET} value calculated by equation 1 in the text. This experiment provided additional evidence that FRET was indeed enhanced in so-designed composite by the Au/SiO_2 NPs in aqueous solution.

Notes and references

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9 R is the distance between the donor and the acceptor point dipoles, R_0 is the Forster radius, κ^2 is the orientation factor, Q_D is the QY of the donor in the absence of the acceptor, J describes the overlap between the normalized emission spectrum of the donor and the molar absorption coefficient of the acceptor, N_A is the Avogadro constant and n is the refractive index of the surrounding medium.