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Electronic Supplementary Information

A Study into the Role of Surface Capping on Energy Transfer in Metal Cluster-Semiconductor Nanocomposites

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Synthesis of Glutathione Capped gold nanoclusters (Au NCs)

We have prepared an aqueous solution of $HAuCl_4$ (20 mM) and Glutathione (10 mM) with millipore water for the synthesis of gold nanoclusters (Au NCs). In a typical synthesis method[1] 0.7 mL millipore water and 6 mL ethanol was taken in a 20 mL beaker and added $HAuCl_4$ (20 mM, 0.50 mL) with vigorous stirring. then aqueous solution of GSH (10 mM, 2 mL) was introduce into the reaction mixture with vigorous stirring for 5 minutes and the reaction mixture turns to cloudy, indicates the formation of Glutathione-Au(I) complexes. The cloudy solution became color less on addition of NaOH solution (1M, 0.6 mL). Finally 0.2mL $NaBH_4$ solution (freshly prepared by dissolving 43 mg of $NaBH_4$ powder in 10 mL of 0.2 M NaOH solution) was added. The GSH-Au_{25}NCs were collected after 3 hours and stored at 4^0C for further characterizations.

Synthesis of L-Cysteine Capped gold nanoclusters (Au NCs)

In a typical synthesis method[1], 4.7 mL millipore water was taken in a 20 mL beaker and then added $HAuCl_4$ (20mM, 0.50 mL) with vigorous stirring. The Cys solution (5mM, 4 mL) was added into the reaction mixture with vigorous stirring for 5 minutes and the reaction mixture turns to cloudy indicating the formation of Cysteine-Au (I) complexes. The cloudy solution became color less on addition of NaOH solution (1M, 0.6 mL). Finally 0.2 mL $NaBH_4$ solution (freshly prepared by dissolving 43 mg of $NaBH_4$ powder in 10 mL of 0.2 M NaOH solution) was added. The Cys-Au_{25}NCs were collected after 3 hours and stored at 4^0C for further analysis.

Synthesis of highly luminescent GSH-capped CdTe QDs:

The synthesis method for GSH-capped CdTe QDs is almost same as earlier illustrated for cysteamine capped CdTe QDs. The synthesis of GSH-capped CdTe QDs has minor modification[2] in experimental parameters. Specifically, the pH of the cadmium precursor solution was attuned to 10.5 by adding drop by drop NaOH (1M).

Results and discussion:

To analyze the PL quenching mechanism the deacy dynamics of CdTe QDs in each nanocomposite have been investigated by time resolved fluorescence spectroscopy. For the Au: Cd ratio 0.02: 1 in GSH-Au_{25}NC-QD nanocomposite the decay time is reduced to 6.87 ns with the combination of 1.19 ns (49%), 7.27 ns (39%), and 28.81 ns (12%). For the Au: Cd ratio 0.16: 1 in GSH-Au_{25}NC-QD nanocomposite the decay time of QDs is reduced to 5.13 ns with the combination of 0.69 ns (61%), 6.37 ns (30%), and 31.15 ns (9%) (Figure S8A). Similarly, for the

Au: Cd ratio 0.02: 1 in Cys-Au_{25}NC-QD nanocomposite the average decay time of CdTe QDs reduced to 6.25 ns with the combination of 1.06 ns (50%), 6.91 ns (39%), and 27.56 ns (11%). For the Au: Cd ratio 0.16: 1 in Cys-Au_{25}NC-QD nanocomposite the average decay time of CdTe QDs reduced to 4.23 ns (Figure S8B). However the decay time of CdTe QDs is drastically changed in BSA-Au_{25}NC-QD nanocomposite. The average decay time of CdTe QDs for Au: Cd ratio 0.02: 1 in BSA-Au_{25}NC-QD nanocomposite is found to be 2.81 ns with the combination of 0.54 ns (81%), 5.52 ns (15%), and 38.71 ns (4%). The decay time of CdTe QDs for Au: Cd ratio 0.16: 1 in same nanocomposite is found to be 1.32 ns with the combination of 0.32 ns (94%), 6.21 ns (5%), and 71.58 ns (1%) (Figure S8C). The decay time of CdTe QDs decreases in presence of Au NCs, which may be due to energy transfer from CdTe QDs to Au NCs.

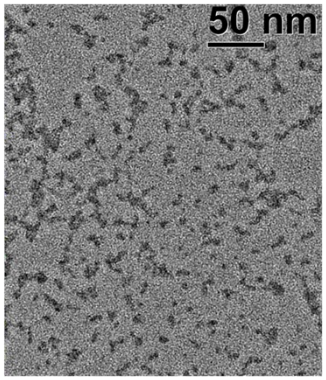

Fig. S1 TEM image of cysteamine capped CdTe QDs.

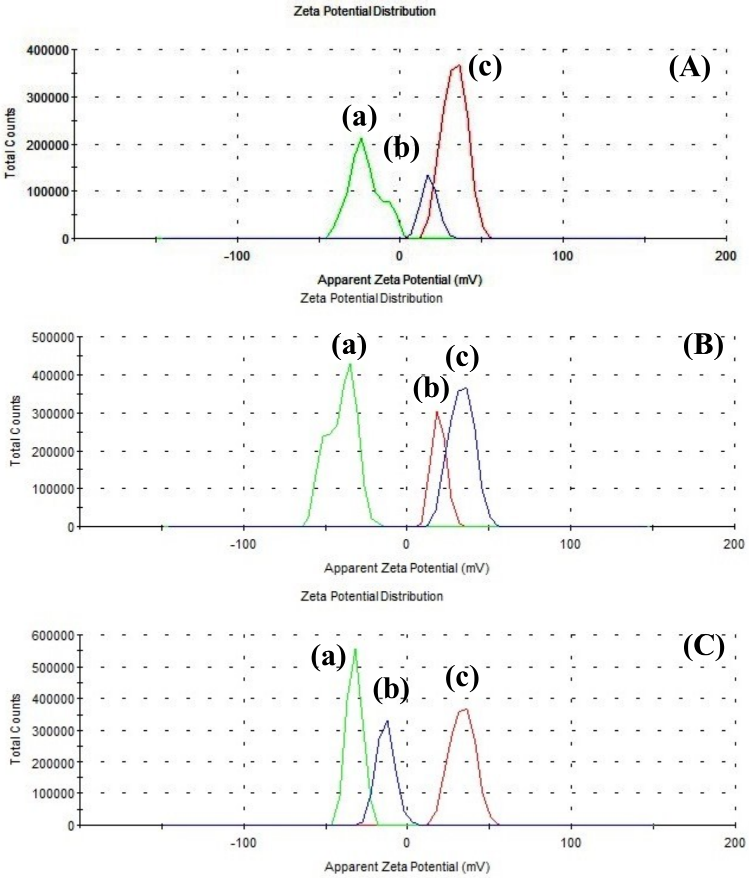

Fig. S2 Zeta potential of (A) GSH-Au_{25}NC (a), GSH-Au_{25}NC-QD (b), CdTe QDs (c); (B) Cys-Au_{25}NC (a), Cys-Au_{25}NC-QD (b), CdTe QDs (c); and (C) BSA-Au_{25}NC (a), BSA-Au_{25}NC-QD (b), CdTe QDs (c), respectively.

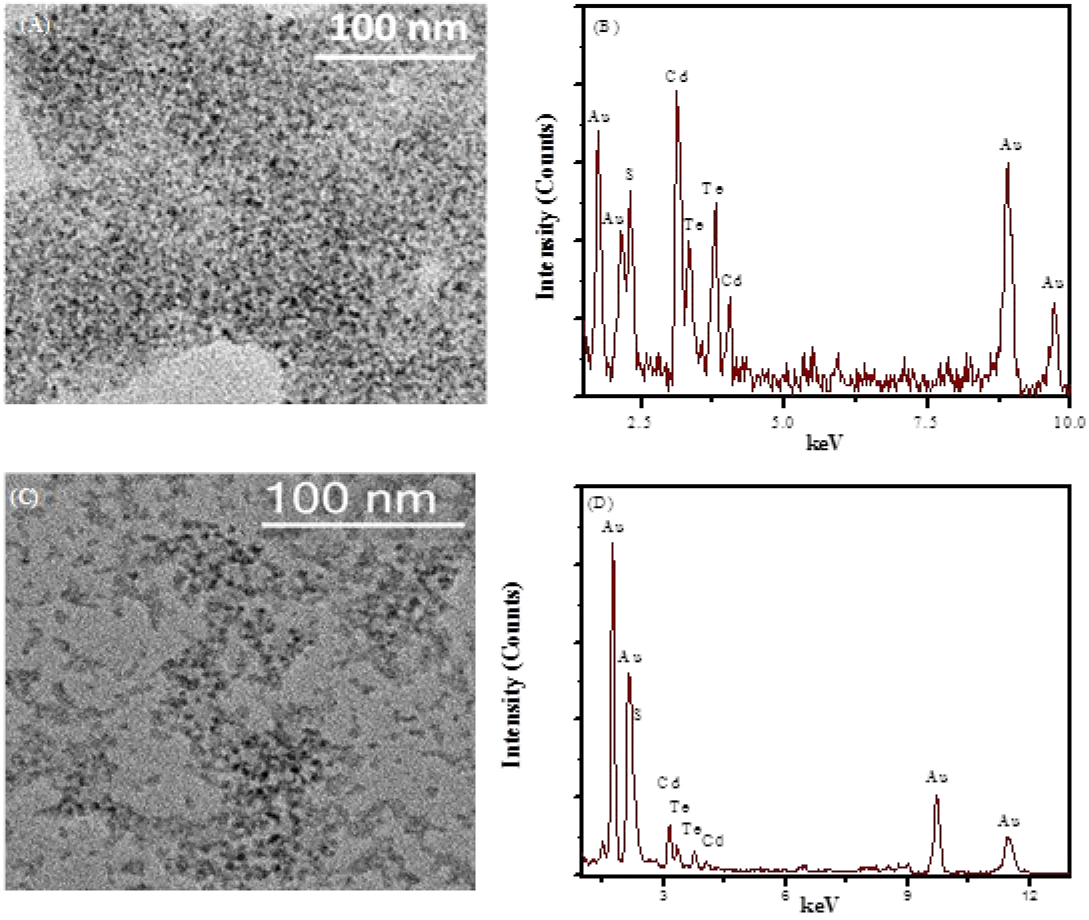

Fig. S3 TEM images (A), (C), and energy dispersive X-ray (EDX) spectra (B), (D) of GSH-Au_{25}NC-QD, Cys-Au_{25}NC-QD, respectively.

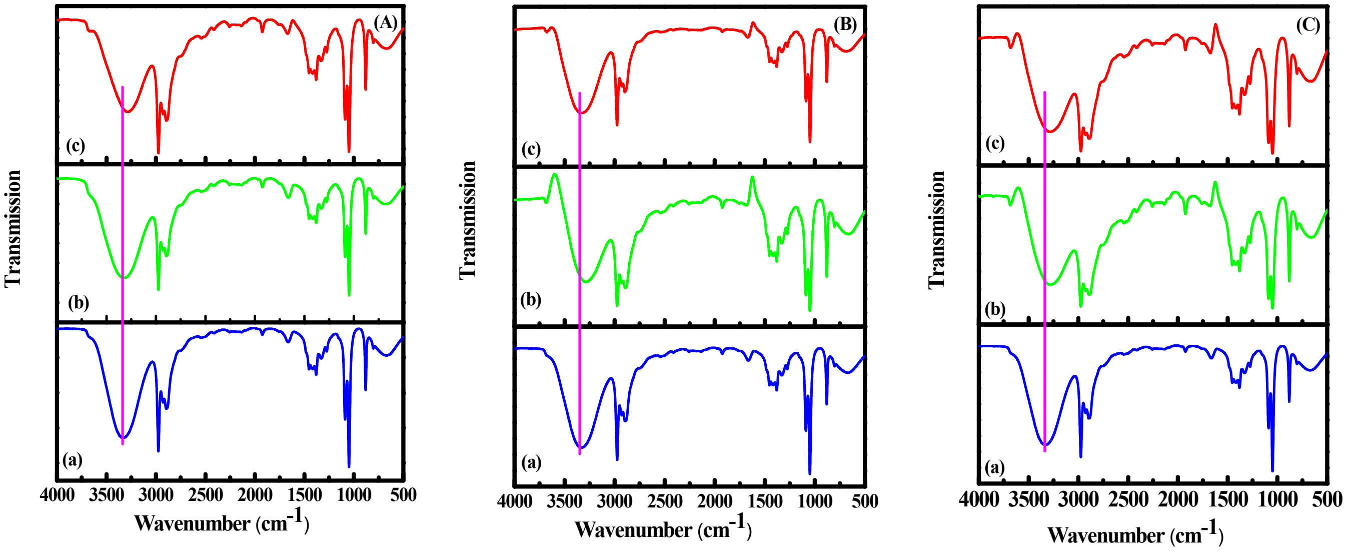

Fig. S4 FTIR spectra of (A) CdTe QDs (a), GSH-Au_{25}NC (b), GSH-Au_{25}NC-QD (c); (B) CdTe QDs (a), Cys-Au_{25}NC (b), Cys-Au_{25}NC-QD (c); and (C) CdTe QDs (a), BSA-Au_{25}NC (b), BSA-Au_{25}NC-QD (c), respectively.

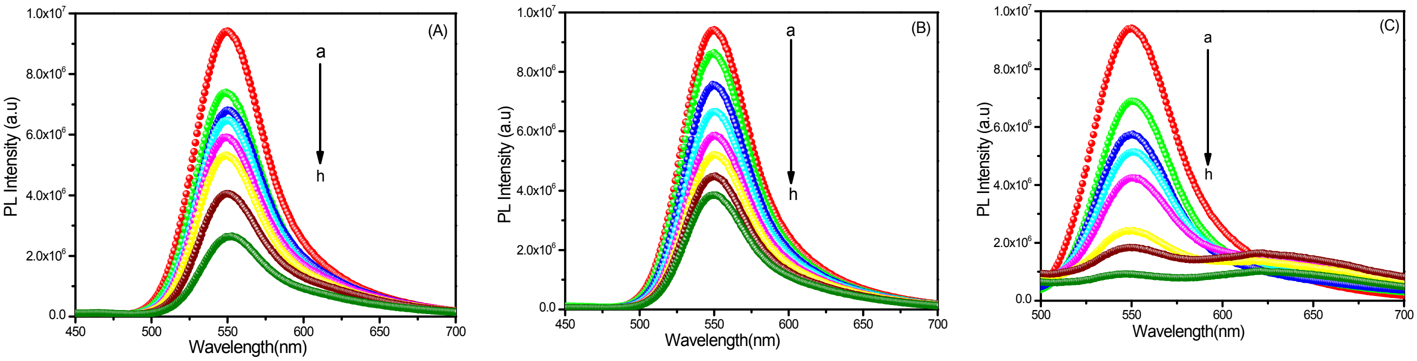

Fig. S5 Photoluminescence spectra of pure CdTe QDs solution in water without Au NCs (a) and nanocomposites with Au: Cd ratio of 0.02: 1 (b), 0.04: 1 (c), 0.08: 1 (d), 0.12: 1 (e), 0.16:1 (f), 0.20: 1 (g), and 0.24: 1 (h) in (A) GSH-Au_{25}NC-QD, (B) Cys-Au_{25}NC-QD, (C) BSA-Au_{25}NC-QD, respectively.

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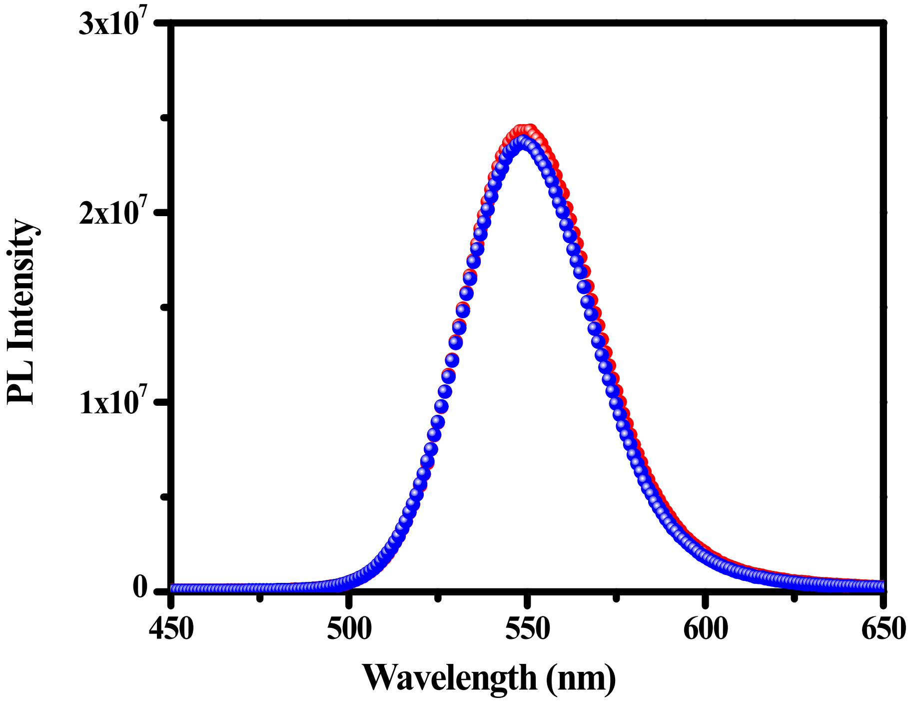

Fig. S6 Photoluminescence spectra of negatively charged glutathione capped CdTe QDs solution in water without Au NCs (red) and in presence of GHS-capped Au_{25}NC with the Au: Cd ratio 0.16: 1 (blue).

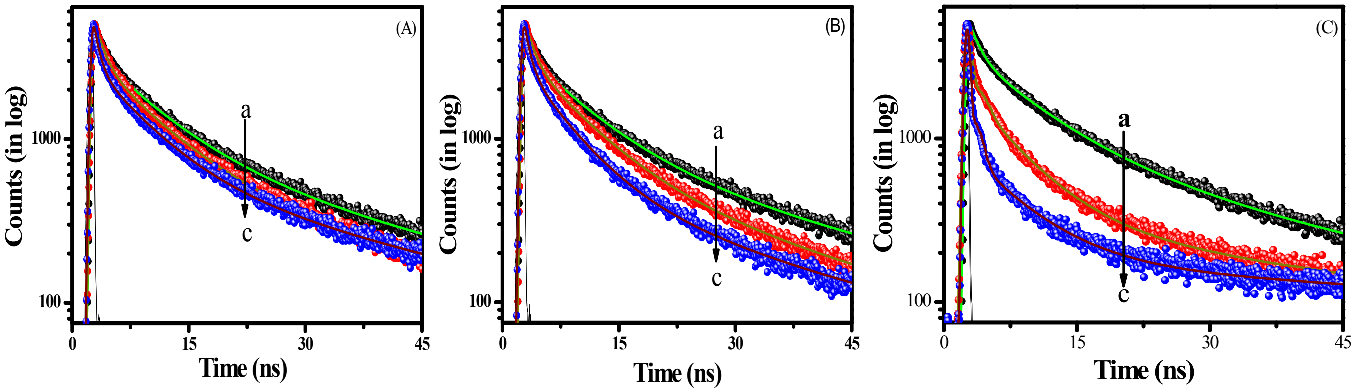

Fig. S7 Time-resolved decay time plots of the CdTe QDs without Au NCs (a) and with Au: Cd ratio 0.02: 1 (b), 0.16:1 (c) in (A) GSH-Au_{25}NC-QD, (B) Cys-Au_{25}NC-QD, (C) BSA-Au_{25}NC-QD, respectively.

References

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2 B. Paramanik, S. Bhattacharyya and A. Patra, *Chem. -Eur. J.*, 2013, **19**, 5980-5987.