Electronic Supplementary Information

Structural Evolution, Photoinduced Energy Transfer in Au Nanocluster–CdTe QD Nanocomposites and Amino Acid Sensing

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Synthesis of GSH capped Au NC

Tripeptide glutathione (GSH, Fig. S1) was used as capping ligand of Au NC. The synthetic procedure for GSH capped Au NC was as follows. In brief, variable amount of chloroauric acid (0.0032 to 0.0064 g i.e. 8.12 µmole to 16.24 µmole) was mixed with 0.046 g GSH (0.15 mmole) in 20 mL argon saturated water with slow stirring. In presence of chloroauric acid, the sulfur group of GSH interacts with Au³⁺ and a white precipitate of Au-GSH complex was formed. After 5 min, 1 (M) NaOH was added to adjust pH 7.0 of the solution. Au-GSH complex became soluble in water due to the deprotonation of carboxylic group in presence of NaOH. This clear solution was allowed to stir for 1h. On heating at 110^oC for 12h, Au-GSH complexes produce Au NC. Noteworthy, one of the major criteria for nanocluster synthesis is high ratio of capping : metal, as described by the previous report.¹ In our synthesis, the concentration of capping ligand is (almost 18.5 times) very high than the concentration of Au. Thus, the average particle sizes of as synthesized Au NC are found to be 1.5 nm in both the cases, such as 8.12 and 16.24 µmole of Au (Fig. S2).

Synthesis of highly luminescent GSH capped CdTe QDs

The synthetic procedure of highly luminescent glutathione capped CdTe QDs was same as Au-CdTe QDs nanocomposite, except the chloroauric acid addition. In brief the synthesis pathway was as follows

Preparation of NaHTe:

In this experiment, 0.0115 g of Te powder was dispersed in 2 mL of argon saturated deionized water in a round bottom flask. The mixture was allowed to stir for 5-7 min to make uniform dispersion of Te powder. 0.01 g of NaBH₄ was added to the mixture and vigorous stirring was continued. After 30 min, solution color was changed from black to faint pink; additionally white thread like precipitation of borax was observed. Faint pink color became dark to darker with time, suggesting the formation of fresh and highly reactive NaHTe. Argon atmosphere was maintained to preserve the highly reactive NaHTe.

Preparation of cadmium precursor:

0.028 g of cadmium chloride hemi-pentahydrate was dissolved in 20 mL of Millipore deionized water in a round bottom flux. After 2 min stirring 0.046 g GSH was added to the Cd^{2+} salt solution under vigorous stirring. Argon gas was bubbled for 15 min to achieve O_2 free condition. Then pH of the solution was raised to 9.2 by adding drop by drop 1(M) NaOH. Then previously prepared NaHTe was immediately injected into the Cd^{2+} solution. The mixture was stirred at room temperature for another 30 min, maintaining argon atmosphere. Finally the solution was heated at 110°C, argon purged condition because CdTe QDs synthesized in inert atmosphere acquired low QY than the QDs prepared in open air condition, keeping other parameteres same. The size tunable emission of QDs could be achieved by changing the heating time, i.e. growth time. The QDs having emission at 523 nm was taken out from the reaction mixture. To remove excess capping ligand the QDs were extensively dialyzed for 8h with changing the water in each 2h. QDs were stored at 4°C for further use and the final concentration of CdTe QDs was fixed at 6.40 X 10⁻⁷ (M) for our experiments. The TEM image of the QDs is given in the Fig.S3 and the average size of the CdTe QDs is found to be 3.1 nm.

The working principle of SAXS

The scattering amplitude follows the Born approximation

$$A(q) = V \int \Delta \rho(r) e^{iq.r} dr$$
(1)
$$a = (A - r) \sum_{i=1}^{n} (20/2)$$
(2)

$$q = (4\pi/\lambda) \cdot \sin(2\theta/2) \tag{2}$$

where A (q), is the scattering amplitude, $\Delta \rho$ is difference in electron density, V is the volume for the integral over the entire medium, q is the scattering vector and λ is the wavelength of the X-ray.

The scattering intensity is related to the scattering amplitude as follows

$$I(q) = A(q) [A(q)]^*$$
 (3)

For the particle having definite shape, the I(q) could be expressed in terms of structural factor [S(q)] and form factor [F(q)], like

$$I(q) = |F(q)|^2 S(q)$$
⁽⁴⁾

There are different expressions of the form factor depending on the shape (spherical, cylindrical, pyramidal etc.) of the particles. We have selected the spherical model for the SAXS analysis because the shape of CdTe QDs and Au NCs are spherical as seen from TEM images. For spherical particle having radius R, the form factor follows the relation

$$[F(q,R)]_{\text{sphere}} = \Delta \rho \cdot [4\pi \{\sin(qR) - qR\cos(qR)\}]/q^3$$
(5)



Fig. S1. The structure of GSH.



Fig. S2. The TEM images of pure Au NC for 8.12 µmole (A) and 16.24 µmole (B) of chloroauric acid, respectively.



Fig. S3. The TEM image of pure CdTe QDs.



Fig. S4. The TEM image of the nanocomposite for 0.07:1 Au:Cd ratio.



Fig. S5. The energy dispersive X-ray (EDX) spectra of Au NC and CdTe (A) for 0.07:1 Au:Cd ratio, (B) for 0.25:1 Au:Cd ratio.



Fig. S6. SAXS profile (A) and size distribution (B) of pure CdTe.



Fig. S7. SAXS profile (A) and size distribution (B) of pure Au NC.



Fig. S8. SAXS profile (A) and size distribution (B) of CdTe QDs in nanocomposite having Au:Cd 0.25:1.



Fig. S9. SAXS profile (A) and size distribution (B) of Au NC in nanocomposite having Au: Cd 0.25:1.



Fig. S10. SAXS profile (A) and size distribution (B) of CdTe QDs in nanocomposite having Au:Cd 0.07:1.



Fig. S11. SAXS profile (A) and size distribution (B) of Au NC in nanocomposite having Au: Cd 0.07:1.



Fig. S12. XPS spectra for the elements of (A) Cd, (B) Te and (C) Au in the physical mixture of pure Au NC and CdTe QDs (having Au:Cd is 0.07:1).



Fig. S13. FTIR spectra of pure GSH, GSH capped CdTe, GSH capped Au NC and the nanocomposite of CdTe and Au NC.



Fig. S14. The absorption spectra of QDs in the nanocomposite, having variable Au: Cd ratio. Pure QDs (represent by 'a' red line), nanocomposites (Au: Cd 0.07: 1, Au: Cd 0.14: 1 and Au: Cd 0.25: 1 are shown by 'b' dark yellow line, 'c' blue line and 'd' green line, respectively) and pure Au NC (shown by 'e' magenta line) are shown different lines.



Fig. S15. Spectral overlap between the absorption of Au NC and emission of CdTe QDs.



Fig. S16. (A) The PL enhancement of nanocomposite (Au:Cd is 0.14:1) probe in presence of different concentrations of L-Cys. (B) The calibration curve of L-Cys to calculate the limit of detection.



Fig. S17. XPS spectra for the elements of (A) Au and (B) S, of the nanocomposite Au:Cd (0.07:1) in presence of L-Cys. The deconvoluted spectrum of S is shown in (C).



Fig. S18. FTIR spectra of the pure L-Cys (a) and the nanocomposite (0.07:1) in absence (b) and presence (c) of L-Cys.



Fig. S19. Decay curves of the nanocomposite (0.07:1) in presence and absence of L-Cys.

Reference

1 Y. Yu, Q. Yao, Z. Luo, X. Yuan, J. Y. Lee and J. Xie, Nanoscale, 2013, 5, 4606-4620.