

Supplementary Information

Modulation of Catalytic Functionality of Alkaline Phosphatase Induced by Semiconductor Quantum Dots: An Evidence of Substrate Mediated Protection

Debasmita Ghosh^a, Chandra Nath Roy^a, Somrita Mondal^a, Somashree Kundu^a, Susmita Maiti^a,
Prasanta Kumar Bag^b and Abhijit Saha^{a*}

^aUGC-DAE Consortium for Scientific Research, Kolkata Centre, III/LB-8 Bidhannagar,
Kolkata 700 098, India

^bDepartment of Biochemistry, University of Calcutta, 35 Ballygunge Circular Road
Kolkata-700 019, India

*Address for correspondence to e-mail: abhijit@alpha.iuc.res.in, fax: +91-33-2335 7008

Synthesis of cysteine-capped CdS quantum dots

CdS QDs, biofunctionalized by surface capping of cysteine, were synthesized following the method as reported earlier.¹ In a typical synthesis of nanoparticles, an aqueous solution (50 ml) Cd²⁺ ions (2.34×10^{-2} M) and L-cysteine (5.85×10^{-2} M) was prepared. pH of the solution was adjusted to 11.2–11.8 by adding NaOH solution (0.1 M) and argon was bubbled through the solution to remove dissolved oxygen. A saturated aqueous solution of H₂S was added to make the final molar ratio of Cd²⁺:cysteine:S²⁻ = 1: 2.5: 0.5. The resultant solution was refluxed and aliquot was collected. Its absorption and luminescence spectra were recorded on UV-Vis absorption (Perkin Elmer Lambda UV/Vis/NIR spectrometer) and luminescence spectrometer (Perkin-Elmer LS-55), respectively.

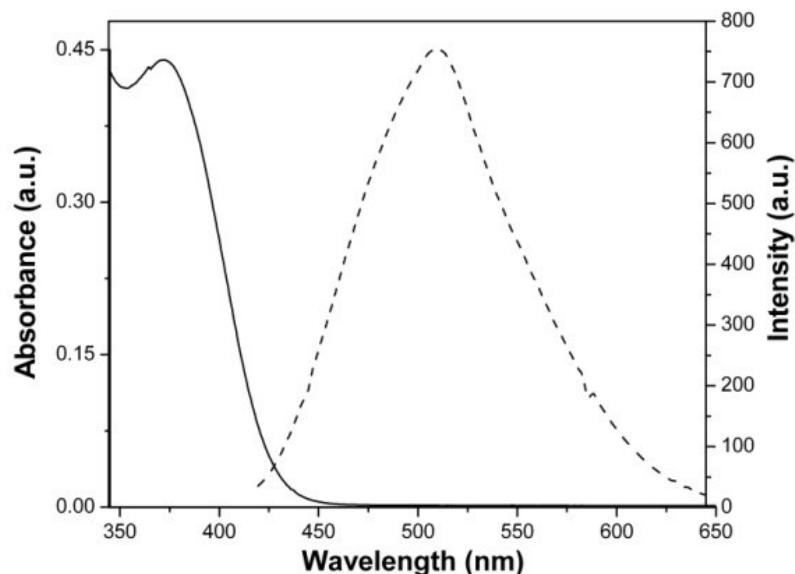


Figure S1. Absorption (—) and luminescence (----) spectra of cysteine-capped CdS quantum dots of average particle size of 3 nm

Synthesis of cysteine-capped CdTe quantum dots

Cysteine capped CdTe QDs were synthesized following the method as reported earlier². NaHTe solution was prepared by reduction of telluric acid with sodium borohydride. An appropriate amount of this solution was taken in a syringe and injected to 50 ml of argon-purged aqueous solution of Cd²⁺– cysteine ($[Cd^{2+}] = 2.34 \times 10^{-2}$ M) having pH in the range of 11.2-11.8. The final molar ratio of Cd²⁺ : cysteine : Te²⁻ was 1 : 2.5 : 0.5. The resultant solution was kept under reflux and aliquot was collected. The optical absorption and emission spectra of the QDs were recorded on UV-Vis absorption (Perkin Elmer Lambda UV/Vis/NIR spectrometer) and luminescence spectrometer (Perkin-Elmer LS-55), respectively.

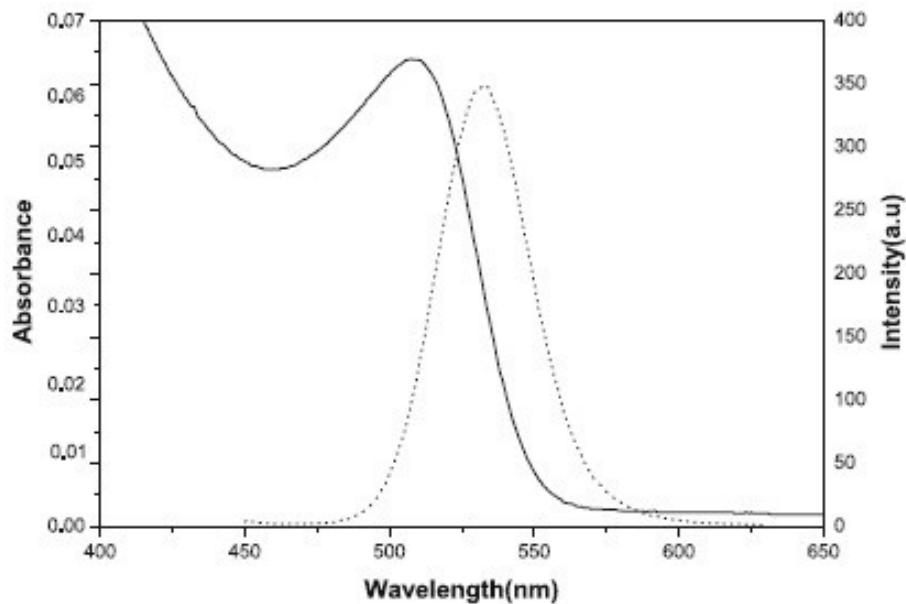


Figure S2. UV-Vis absorption (—) and photoluminescence (·····) spectra of cysteine capped CdTe QDs (average size 3 nm)

Synthesis of BSA-capped CdS quantum dots

CdS QDs, biofunctionalized by surface capping of BSA, were synthesized following the method as reported earlier.³ An aqueous solution containing Cd²⁺ ions and BSA of appropriate amount ([BSA] = 3 mg/ml and [Cd²⁺] = 2.34×10^{-2} M) was prepared and foam was generated while nitrogen was bubbled through the solution to remove dissolved oxygen. An aqueous solution of Na₂S (1×10^{-3} M) was added into the mixture and a yellow colored solution of CdS NPs was obtained. The final molar ratio of Cd²⁺:S²⁻ was kept at 1:0.5. The reaction system was left at 25 °C for overnight. The optical absorption and emission spectra of the QDs were recorded on UV-Vis absorption (Perkin Elmer Lambda UV/Vis/NIR spectrometer) and luminescence spectrometer (Perkin-Elmer LS-55), respectively.

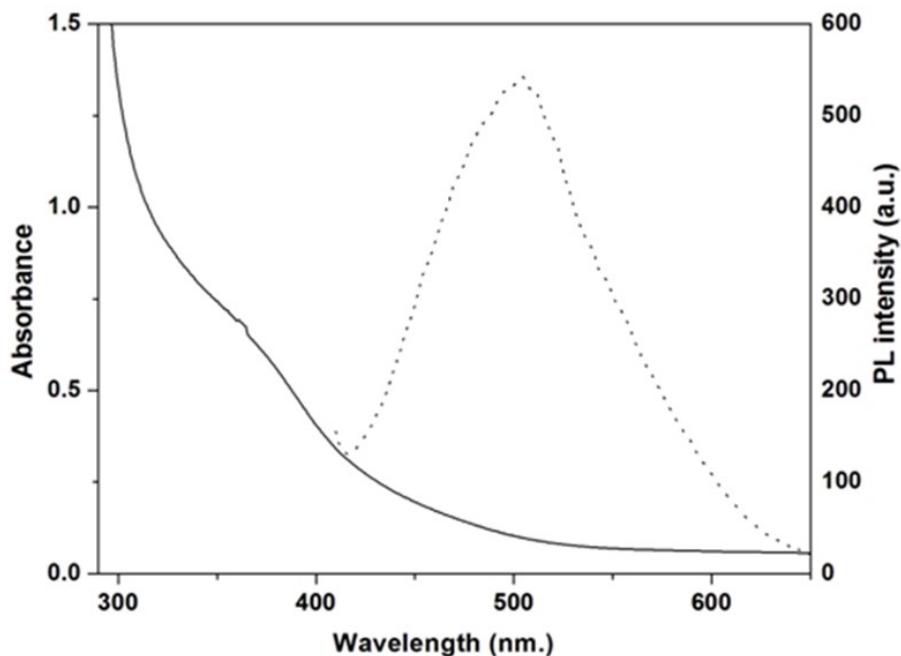


Figure S3. UV-Vis absorption (——) and photoluminescence (·····) spectra of BSA capped CdS QDs

Determination of average particle size

Semiconductor nanoparticles exhibit a blue shift in the absorption spectra as the size is reduced below the characteristic Bohr exciton diameter of the bulk material.⁴ The quantitative relationship between absorption spectra and particle size is now well understood.⁵ The band gap (E_g) was calculated from absorption onset (λ_{onset}) in the UV-Vis absorption spectra of each nanoparticle solution using the relation $E_g = hc/\lambda_{onset}$, where h is the Planck's constant and c , the speed of light. The average size of nanoparticles (d) was obtained using the correlation of band gap shift ($\Delta E_g = E_g(nanocrystal) - E_g(bulk)$) and particle size deduced by tight-binding approximation⁵ (eq. (S1)).

$$\Delta E_g = a_1 e^{-d/b_1} + a_2 e^{-d/b_2} \quad (S1)$$

The values of the parameters for CdS QDs are $a_1 = 2.83$, $b_1 = 8.22$, $a_2 = 1.96$, $b_2 = 18.07$ and that for CdTe QDs are $a_1 = 5.77$, $b_1 = 8.45$, $a_2 = 1.33$, $b_2 = 43.73$.

The particle sizes determined by this optical method were 3 and 3.2 nm for cys-CdTe and cys-CdS, respectively.

TEM measurements:

Typical TEM images for cysteine capped CdS and CdTeQDs are shown in Fig.S4.

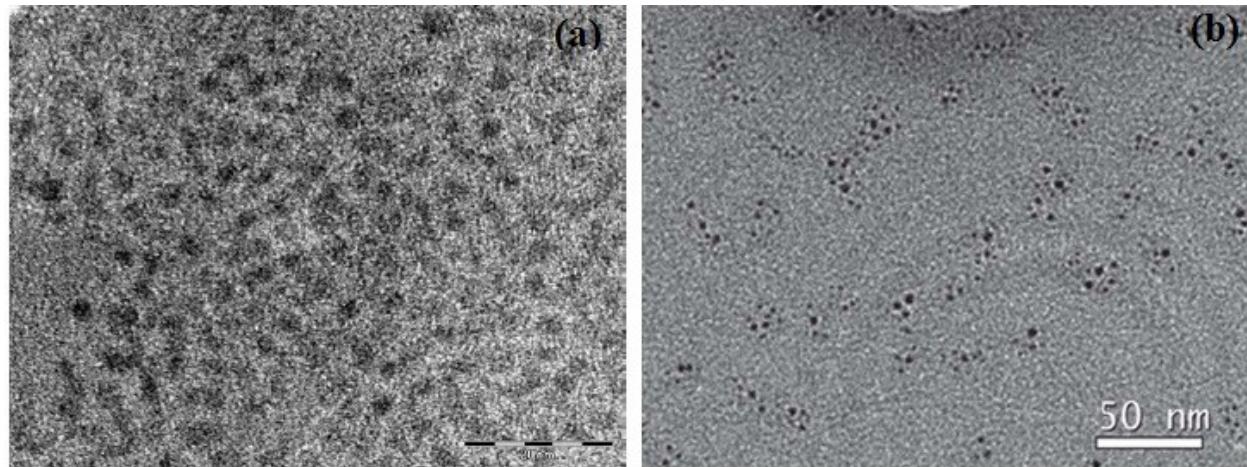


Figure S4. TEM images of cysteine capped (a) CdTe and (b) CdS NPs

The QDs are approximately spherical in shape. The average particle sizes determined are 3 nm for CdTe and 3.2 nm for CdS QDs.

Dynamic light scattering (DLS)

Size distribution measurements of the nanoparticles were made by dynamic light scattering (Model DLS-nanoZS, Zetasizer, Nanoseries, Malvern Instruments). Samples were filtered several times through a 0.22 mm Millipore membrane filter prior to measurements.

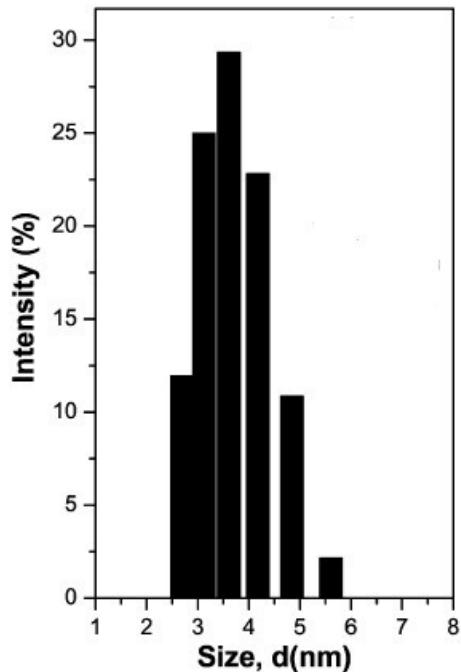


Figure S5: A typical size distribution histogram obtained by dynamic light scattering (DLS) for CdS QDs

The average particle size of cys-CdS QDs determined by DLS measurements is 3.6 nm, which is slightly larger than the sizes determined by UV-vis absorption spectroscopy. This is consistent with the established notion that it is the hydrodynamic diameter of the colloidal particles that gets measured by DLS technique. However, the average particle size determined from TEM image (Fig. S4) for CdS QDs is in good agreement with the data obtained by UV-vis absorption spectroscopy.

Determination of particle concentration

Band gap was calculated from absorption onset in the UV-Vis absorption spectra of each nanoparticle solution. The average particle size of quantum dots was obtained from the correlation of bandgap and particle size deduced by tight-binding approximation.⁵ Concentrations of QDs were calculated using the correlation of molar extinction coefficient with particle diameter⁶ and absorbance values observed for the respective QD solution.

Fluorescence lifetime measurements

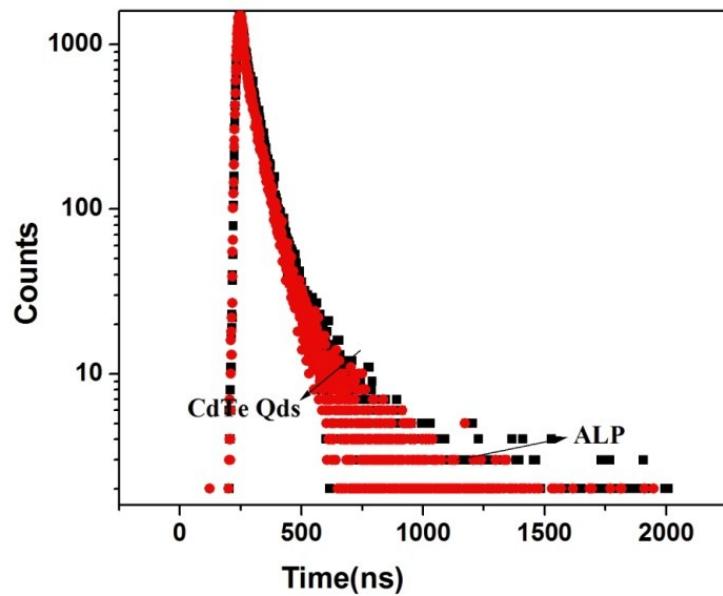


Figure S6. A typical decay profile of ALP in presence of CdTe QDs

Table S1: Change in activity and kinetic parameters of ALP in presence of BSA-CdS QDs when QDs were mixed with enzyme before addition of substrate

Concentrations of BSA-CdS (nM)	% activity remaining	K _m (M)	V _{max} (μ moles min ⁻¹)
0	100	5.46×10 ⁻⁴	44.24
10	90	5.22×10 ⁻⁴	42.68
50	88	4.93×10 ⁻⁴	40.43
100	84	4.72×10 ⁻⁴	39.46

References

1. A. Priyam, S. Ghosh, S.C. Bhattacharya, and A. Saha, *J. Colloid Interf. Sci.* 2009, **333**, 195-201.
2. A. Priyam, A. Chatterjee, S. C. Bhattacharya, and A. Saha, *J. Cryst. Growth.* 2007, **304**, 416–424.
3. D. Ghosh, S. Ghosh, S. Mondal, and A. Saha, *J. Mater. Chem.* 2012, **22**, 699-706.
4. M. Bruchez, M. Moronne, P. Gin, S. Weiss and A. P. Alivisatos, *Science*, 1998, 281, 2013.
5. S. Sapra and D. D. Sarma, *Phys. Rev. B: Condens. Mater. Phys.*, 2004, 69, 125304.
6. W.W. Yu, L. Qu. W. Guo and X. Peng. *Chem. Mater.* 2003, **15**, 2854–2860.