

Organic-Free Colloidal Semiconductor Nanocrystals as Luminescent Sensors for Metal Ions and Nitroaromatic Explosives

Abhishek Swarnkar, G. Shiva Shanker, Angshuman Nag*

Department of Chemistry, Indian Institute of Science Education and Research (IISER),
Pune, India – 411008

*Corresponding author's e-mail: angshuman@iiserpune.ac.in

Electronic Supplementary Information (ESI)

Chemicals:

Cadmium oxide (99.995%, Aldrich), zinc oxide ($\geq 99\%$, Aldrich), oleic acid (90%, technical grade, Aldrich), 1-Octadecene (90%, Aldrich), sulfur (99.998%, Aldrich), selenium (99.99%, Aldrich), trioctylphosphine (TOP, 97%, Aldrich), formamide (FA, spectroscopy grade, Aldrich), hexane (AR, S D Fine chem. Ltd), ammonium sulfide (40-48 wt% solution in water, Aldrich), toluene (99.5%, Rankem), ethanol (99.9% AR, S D Fine chem. Ltd), N,N-dimethyl formamide (DMF dry, S D Fine chem.), trimethyloxonium tetrafluoroborate (95%, Aldrich), cadmium nitrate tetrahydrate (98%, Aldrich), zinc nitrate hexahydrate (98%, Aldrich), HEPES sodium salt (99.99%, Sigma), potassium nitrate ($\geq 99\%$, Aldrich), nickel(II) nitrate hexahydrate (98%, Merck), cobalt(II) nitrate hexahydrate ($\geq 97\%$, Merck), indium(III) nitrate hydrate (99.999%, Aldrich), manganese(II) nitrate hydrate (98%, Aldrich), iron(III) nitrate ($\geq 98\%$, Merck), barium(II) nitrate (99%, Merck), magnesium nitrate hexahydrate (99.0%, S D Fine chem. Ltd), mercury(II) nitrate monohydrate ($\geq 98\%$, Aldrich), lead(II) nitrate ($\geq 99\%$, Aldrich), 3-Mercaptopropionic acid (MPA, $\geq 99\%$, Aldrich), toluene (99.8%, Aldrich), acetonitrile (dry, S D Fine chem. Ltd.), 4-nitrotoluene (99%, Aldrich), 2,4-dinitrotoluene (2,4-DNT, 99%, Aldrich), 2,6-dinitrotoluene (2,6-DNT, 99%, Aldrich), 2,4,6-

trinitrophenol (TNP, 99%, Aldrich). All the Chemicals were used as received without further purification.

Synthesis of Oleic Acid Capped CdSe/CdSeS/CdS core/gradient-shell/shell Nanocrystals (NCs):

The synthesis was carried out following Sarma et al.¹ 0.0496 g CdO, 0.5 mL of oleic acid and 10 mL 1-Octadecene was degassed (under alternate vacuum and nitrogen) at 120 °C for 30 minutes at mild stirring rate. The temperature of reaction mixture was increased up to 300 °C forming a clear solution. 1 mL TOP solution containing sulfur (0.0128 g) and selenium (0.0016 g) is then quickly injected to the uniformly stirred Cd solution at 300 °C. The reaction was carried out for 20 seconds. While cooling down to room temperature, the reaction mixture was diluted with ~10 mL toluene at ~100 °C. Precipitation of NCs was carried out by addition of minimum amount of ethanol, followed by centrifugation. The wet NC pellet obtained after centrifugation was redispersed in toluene and precipitated using ethanol. The same process of dispersion/precipitation was repeated once more. Figure S1 shows the absorption and emission spectra of obtained NCs dispersed in toluene. The obtained PL quantum yields are typically in the range of 50-70%.

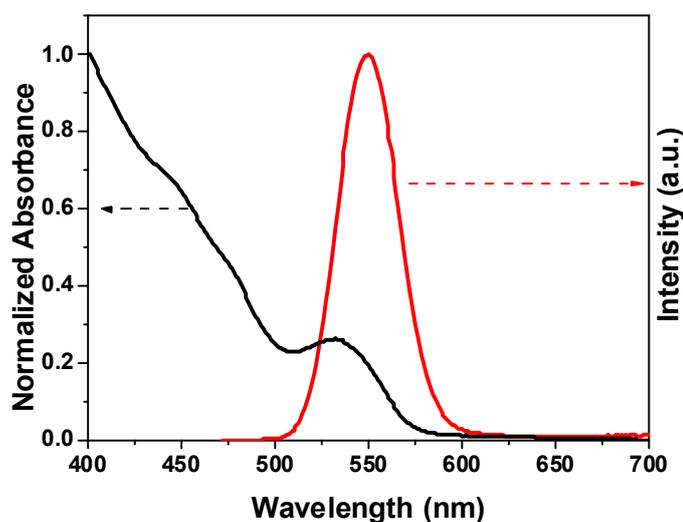


Figure S1: UV-visible absorption and photoluminescence spectra of oleic acid capped CdSe/CdSeS/CdS core/gradient-shell/shell NCs.

Synthesis of Oleic Acid Capped CdSe/CdS-ZnS Core/Hybrid-Shell NCs:

The synthesis was carried out following ref.² 0.0496 g CdO, 0.0496 g ZnO, 2 mL of oleic acid and 10 mL 1-Octadecene was degassed (under alternate vacuum and nitrogen) at 120 °C for 30 minutes at mild stirring rate. The temperature of reaction mixture was increased up to

310 °C forming a clear solution. 1 mL TOP solution containing sulfur (0.0567 g) and selenium (0.0075 g) is then quickly injected to the uniformly stirred Cd solution kept at 310 °C. The reaction was carried out for 1 minute. While cooling down to room temperature, the reaction mixture was diluted with ~10 mL toluene at 100 °C. Precipitation of NCs was carried out using ethanol followed by centrifugation. The NCs were redispersed in toluene and again precipitated with ethanol. The process of redispersion/precipitation was repeated once more. Figure S2 shows UV-visible absorption and PL data of obtained NCs dispersed in toluene.

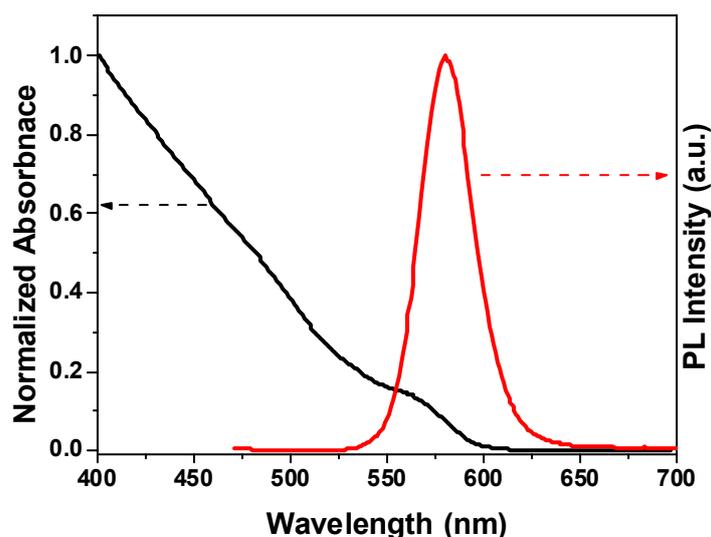


Figure S2: UV-visible absorption and photoluminescence spectra of oleic acid capped CdSe/ZnS-CdS core/hybrid-shell NCs.

Ligand Exchange with S²⁻:

Organic ligand was exchanged with S²⁻ following ref.³ where 1 mL FA was added to 1 mL oleic acid- capped NCs dispersed in toluene and then 10 μ L aqueous solution (40-48 wt %) of ammonium sulfide was added to the FA layer. Vigorous stirring of the two phases for about 10 min led to a complete phase transfer of NCs in to FA from toluene phase. The color-less toluene phase was discarded followed by the addition of fresh toluene in order to wash out any residual organic molecules from the FA phase. The washing was repeated for two more times. NCs dispersed in FA were precipitated by using minimum amount of acetonitrile (~0.8 mL) followed by centrifugation. The obtained precipitate of S²⁻ capped NCs can be redispersed in a polar solvent like FA and water. For metal ion sensing, the NC precipitate was re-dispersed in aqueous solution of HEPES buffer where pH was buffered at 7.4 (physiological pH). In some experiments the precipitate was redispersed in FA. PL quantum yield of S²⁻ capped NCs typically decreases to ~1% after the ligand exchange.

Ligand Exchange with MPA: Ligand exchange with MPA was carried out similar to that with $(\text{NH}_4)_2\text{S}$ but with a different ligand. MPA was used instead of $(\text{NH}_4)_2\text{S}$.

Ligand Stripping with Trimethyloxonium Tetrafluoroborate:

Stripping of organic ligand was done with trimethyloxonium tetrafluoroborate following the report of Helms et al.⁴ Oleic acid capped CdSe/CdS-ZnS core/hybrid-shell NCs were redispersed in 1 mL hexane (~5 mg/mL). 1 mL DMF was added to the NC dispersion in hexane, followed by addition of appropriate amount of trimethyloxonium tetrafluoroborate to the DMF layer. Vigorous stirring of the two phases for about 5 minutes led to a complete phase transfer of NCs to DMF from hexane phase. The NCs dispersed in DMF was washed thrice with fresh hexane and then separated out by discarding the upper hexane phase. NCs were precipitated by adding toluene to DMF phase. The resulting precipitate was re-dispersed in DMF.

Preparation of Buffer Solution:

10 mM HEPES buffer solution was prepared by dissolving 1.3015 g HEPES-Na salt (4-(2-Hydroxyethyl) piperazine-1-ethanesulfonic acid sodium salt,) in 500 mL water and then pH was adjusted to 7.4 by drop-wise addition of aqueous solution of 1N HCl.

Sensing of Metal Ions:

Aqueous solutions (0.1 mM) of KNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3$, $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ were added one by one to the S^{2-} capped CdSe/CdSeS/CdS NCs dispersed in the buffer solution maintained at pH 7.4. Concentration of NC was adjusted such that the optical density at the lowest energy excitonic peak is 0.1. Influence of different metal ion on the NC emission was studied by measuring PL spectra after exciting at 450 nm. After noticing that the addition of Cd^{2+} ion increases the NC PL significantly, we measured the PL of NC after adding different concentrations of Cd^{2+} ions.

Sensing of Nitroaromatic Compounds:

Five nitroaromatic compounds- nitrobenzene, 4-nitrotoluene, 2,4-DNT, 2,6-DNT and TNP were selected to search their interaction with S^{2-} capped and ligand-free CdSe/CdS-ZnS core/hybrid-shell NCs. 0.1 mM aqueous solutions of each nitroaromatic compounds were added one by one to the aqueous solution NCs with absorbance of lowest energy excitonic

peak maintained at 0.1. PL spectra were measured subsequently corresponding to each nitroaromatic compound after excitation at 450 nm. Since TNP was found to influence NC PL, we titrated NC dispersion with different concentrations of TNP and measured PL at each concentration.

Instrumentation:

UV-visible absorption and PL spectra of NCs were recorded using a Perkin Elmer, Lambda-45 UV/Vis spectrometer and FluoroMax-4 spectrofluorometer (HORIBA scientific), respectively. PL decay dynamics were measured using time correlated single photon counting (TCSPC) technique set up from Horiba JobinYvon at excitation energy of 459 nm. PL decays were measured for oleic acid capped NCs dispersed in toluene and S^{2-} capped, and Cd^{2+} treated S^{2-} capped NCs were dispersed in the aqueous buffer with pH 7.4. ζ -potential were obtained employing Henry's equation in the Smoluchowski limit, using a Zetasizer Nano series, Nano-ZS90 (Malvern Instruments, U.K.). Isothermal Calorimetry (ITC) was done using MicroCal iTC200 system (GE Healthcare Life Sciences). NCs dispersed in FA were kept in the titration cell as a titer and was titrated by Cd^{2+} solution in FA. Both the titrant (Cd^{2+} ions) and the NCs were dispersed in formamide, sonicated and filtered through 0.45 μm PTFE filter. Temperature of the titration cell was maintained at 298 K and ITC curve was the result of the average of nearly three successive titrations which included the subtraction of FA dilution binding energetic. Molar concentration of NCs was calculated following the report by Peng et al.⁵ Fourier-transform infrared (FTIR) spectroscopy was carried out in the transmission mode using a NICOLET 6700 FTIR spectrometer (Thermo scientific).

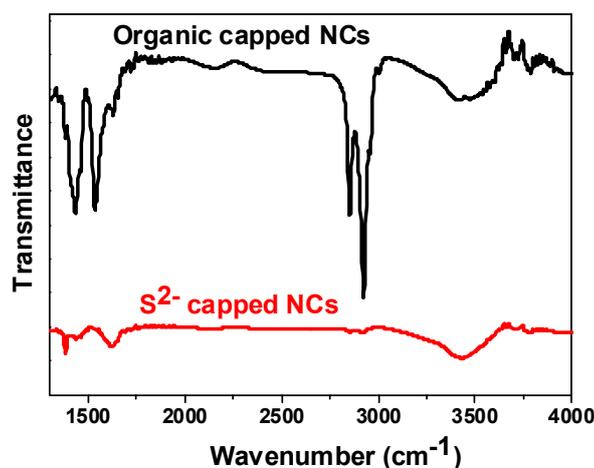


Figure S3: Comparison of FTIR spectra of organic and S^{2-} capped CdSe/CdSeS/CdS core/gradient-shell/shell NCs. Similar weights of both NC samples were taken for FTIR measurements. Absence of two bands $\sim 2900\text{ cm}^{-1}$ indicates the absence organic ligands.³

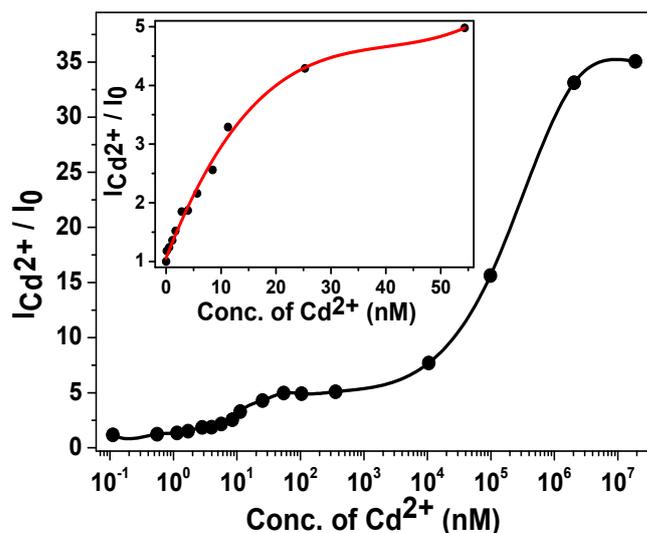


Figure S4: Plot of relative intensity ($I_{Cd^{2+}}/I_0$) of S^{2-} capped CdSe/CdSeS/CdS NCs against concentration of added Cd^{2+} ion. Closed circles are experimental data and the line is just a guide to eye. Inset shows same plot of $I_{Cd^{2+}}/I_0$ against concentration of Cd^{2+} ions, but for lower concentration range of Cd^{2+} ions; the red line is a polynomial fit to the experimental data shown by closed circle. Excitation wavelength for all the spectra was fixed at 450 nm.

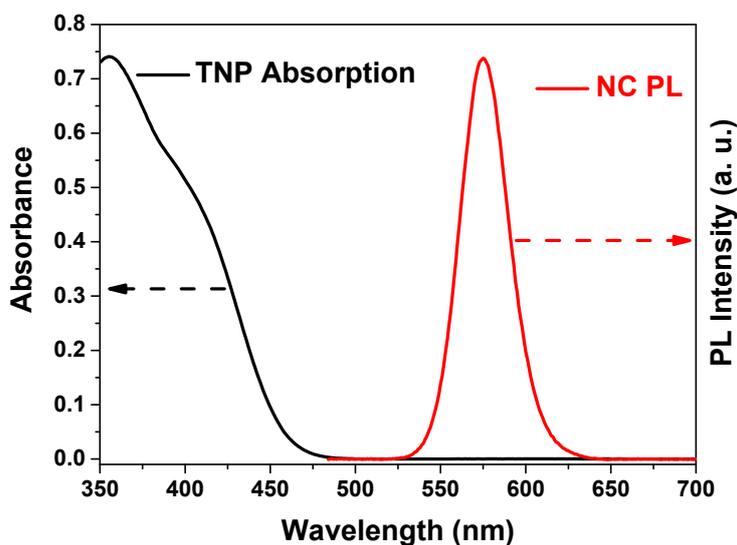


Figure S5: UV-visible absorption spectrum of TNP, and PL spectrum of S^{2-} CdSe/CdS-ZnS core/hybrid-shell NCs. There is no spectral overlap between NC emission and TNP absorption.

References:

- (1) D. D. Sarma, A. Nag, P. K. Santra, A. Kumar, S. Sapra and P. Mahadevan, *J. Phys. Chem. Lett.*, 2010, **1**, 2149.
- (2) A. Nag, A. Kumar, P. P. Kiran, S. Chakraborty, G. R. Kumar and D. D. Sarma, *J. Phys. Chem. C*, 2008, **112**, 8229.
- (3) A. Nag, M. V. Kovalenko, J. S. Lee, W. Y. Liu, B. Spokoyny and D. V. Talapin, *J. Am. Chem. Soc.*, 2011, **133**, 10612.
- (4) E. L. Rosen, R. Buonsanti, A. Llordes, A. M. Sawvel, D. J. Milliron and B. A. Helms, *Angew. Chem.-Int. Edit.*, 2012, **51**, 684.
- (5) W. W. Yu, L. H. Qu, W. Z. Guo and X. G. Peng, *Chem. Mat.*, 2003, **15**, 2854.