

Silver Nanoparticle Film Induced Photoluminescence Enhancement of Near-infrared Emitting PbS and PbS/CdS Core/shell Quantum Dots: Observation of Different Enhancement Mechanisms

H.Y. Liang,^a H.G. Zhao,^{*a} Z.P. Li,^b C. Harnagea,^a and D.L. Ma^{*a}

^aInstitut National de la Recherche Scientifique, University of Québec, 1650 Boulevard Lionel-Boulet, Varennes, Québec, J3X 1S2 Canada.

^bBeijing Key Laboratory of Nano-Photonics and Nano-Structure (NPNS), Department of Physics, Capital Normal University, Beijing, 100048 China

* Corresponding authors: zhaoh@emt.inrs.ca and ma@emt.inrs.ca

Experiments

Materials

Lead chloride (98%), sulfur (100%), oleylamine (OLA) (technical grade, 70%), cadmium oxide (99%), oleic acid (OA), octadecene (ODE), ethylene glycol (EG), NaSH, silver trifluoroacetate, AgNO₃ (99.8%) and poly(vinyl pyrrolidone) (PVP) with an average molecular weight of 40,000 (PVP K30), polymethylmethacrylate (PMMA) with an average molecular weight of 120,000 were obtained from Sigma-Aldrich Inc. Polyethylene glycol 600 (PEG 600) was purchased from Xilong Chemical Industry Incorporated Co. LTD. Hexane, toluene, chloroform and ethanol were purchased from Fisher Scientific Company. All chemicals were used as purchased.

Synthesis of PbS QDs

PbS QDs were synthesized by using OLA as ligands.^{1,2} Typically, PbCl₂ (3.6 mM) in OLA (2.4 mL) and sulfur (0.36 mM) in OLA (0.24 mL) were purged, respectively, by N₂ at room temperature for 30 min. The PbCl₂-OLA suspension was then heated to 160 °C and kept at this temperature for 1 hour. Subsequently, the PbCl₂-OLA suspension was cooled to 120 °C under vacuum for 15 min. The flask was then reopened and the N₂ flux was restored. Sulfur in OLA at room temperature was quickly injected into the PbCl₂-OLA suspension under vigorous stirring. The reaction cell was quenched with cold water after the growth reaction was conducted at 100 °C for 1–360 min to obtain PbS QDs of different sizes. Alcohol was added, and then the suspension was centrifuged and supernatant was removed. The QDs were re-dispersed in toluene or chloroform.

Synthesis of PbS/CdS QDs

PbS/CdS QDs with a thin shell were synthesized via a cation exchange method.³ Typically, CdO (2.3 mM), OA (2 mL) and ODE (10 mL) were heated to 255 °C under N₂ for 20 min. The clear solution was cooled to 155 °C under vacuum for 15 min. The flask was then reopened and the N₂ flux was restored. PbS QDs suspension in toluene (1 mL, Absorbance = 3 at the first excitation peak)

was diluted in 10 mL toluene, bubbled for 30 min and then heated to 100 °C immediately. The Cd/OA mixture was injected. The reaction cell was quenched with cold water after the growth reaction was conducted at 100 °C for different time. Alcohol was added, and then the suspension was centrifuged and supernatant was removed. The QDs were dispersed in toluene or chloroform.

Synthesis of Ag Nanoparticles (NPs)

The NPs with the surface plasmon resonance (SPR) peak at 420 nm (Ag#1) were synthesized via the protocol reported by Xia, *et al.*⁴ Typically, EG (5 mL) was added into a 50 mL round bottom flask and heated under magnetic stirring at 150 °C. NaSH (60 µL; 3 mM in EG) was quickly injected into the heated solution. Two minutes later, a 3 mM HCl solution (0.5 mL) was injected into the heated reaction solution, followed by the addition of PVP (1.25 mL, 20 mg/mL in EG). After another 2 min, silver trifluoroacetate (0.4 mL, 282 mM in EG) was added into the mixture. The reaction time was 10 min. The reaction solution was quenched by placing the reaction flask in an ice-water bath. All the samples were collected by centrifugation and then washed with acetone once to remove the remaining precursor and EG, and then alcohol four times to remove excess PVP. The Ag NPs were dispersed into alcohol.

The NPs with the SPR peak at 450 nm (Ag#2) were synthesized via a slightly modified polyol protocol by using PEG both as solvent and reduction agent.⁵⁻⁷ Typically, PVP (1.11g) was dissolved in 100 mL of PEG under stirring, followed by the addition of 1 mL of 2 M AgNO₃ aqueous solution. Then the solution was heated to and kept at 70 °C in an oil bath for ~2 h. When the yellow color disappeared, the nearly-colorless solution was further heated at 80 °C for 16h. The sample was collected by centrifugation and then washed with acetone once to remove the remaining precursor and PEG, and then washed with alcohol for four times to remove excess PVP. The NPs were dispersed into alcohol for further investigation.

Preparation of QDs/Ag films

Firstly, we attached Ag NPs (SPR peak located at ~420 nm or ~450 nm) to ITO-coated glass slides by drop casting, and then over coated them with a thin layer of PMMA via spin coating (0.5% PMMA in chloroform, 3000 revolutions per min (RPM), 1 min). After that the QDs suspended in 0.1% PMMA in chloroform were further deposited on the PMMA film via spin coating (two steps: 1500 RPM, 5s and then 2500 PRM, 40s).

Characterizations

PbS and PbS/CdS QDs were characterized by a JEOL 2100F transmission electron microscopy (TEM). Scanning electron microscopy (SEM) images of silver NPs were obtained using a

HITACHI S-4800 SEM. Absorption spectra were acquired with a Cary 5000 ultraviolet (UV)-Vis-near-infrared (NIR) spectrophotometer (Varian) with a scan speed of 600 nm/min. Fluorescence spectra were taken with a Fluorolog®-3 system (Horiba Jobin Yvon). The xenon lamp was used to excite the QDs for steady state measurements. Fluorescence life time of PbS/CdSQDs was measured using a pulsed laser diode of 444 nm or 636 nm and fast multichannel scaler mode in the Fluorolog®-3 system. The repetition rate is 100 k and spot diameter of the excitation laser on the sample is around 1 mm. The decay curves were analyzed using DAS 6 software. Dye IR 125 dissolved in dimethyl sulfoxide was used as a reference for QY measurements.

Table S1 Emission peak position (nm) and QY of investigated PbS and PbS/CdS core/shell QDs measured in toluene.

Samples	λ_{em} (nm)	QY (%)
PbS#1	1100	85
PbS#2	1320	40
PbS#3	1400	26
PbS#4	1500	19
PbS/CdS#1	1190	52
PbS/CdS#2	1350	49
PbS/CdS#3	1460	36

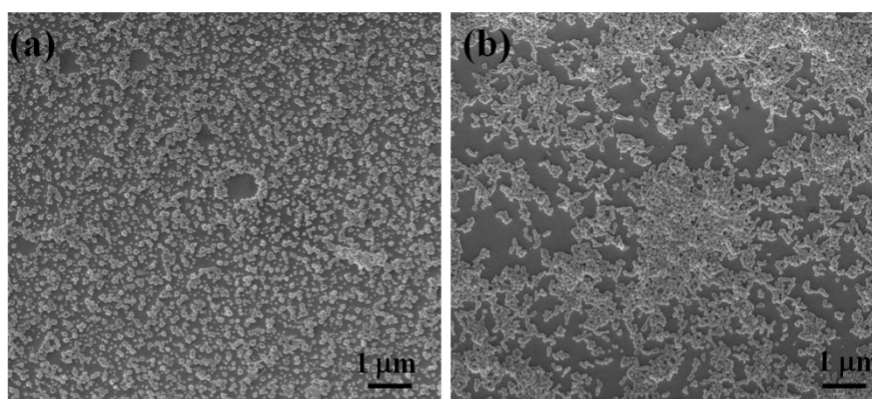


Fig. S1 SEM images of (a) Ag#1 and (b) Ag#2.

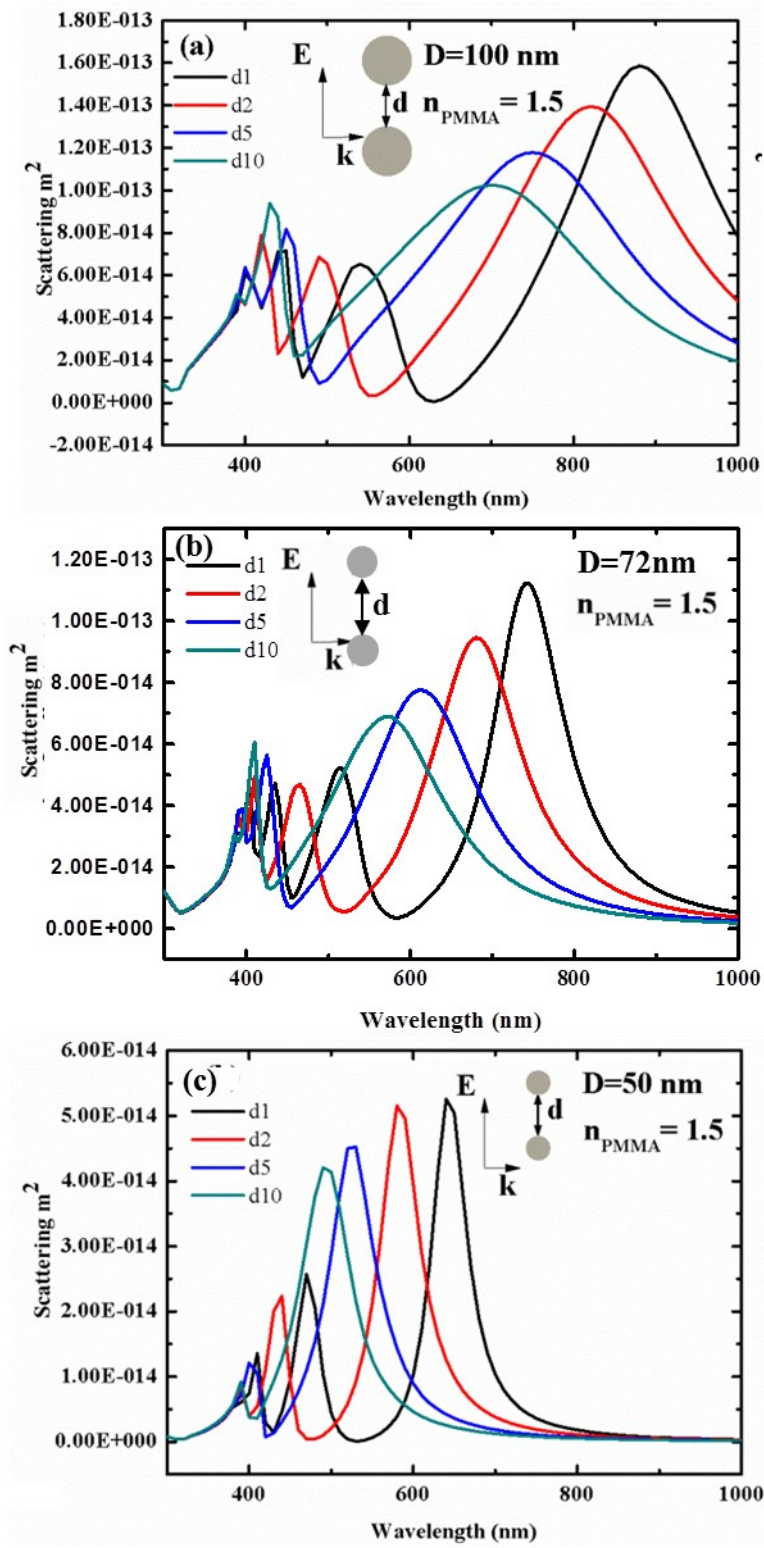


Fig. S2 Calculation of the scattering by coupled spheres at different separation distances: $d=1, 2, 5, 10 \text{ nm}$. The diameters of spheres are 100 nm in (a), 72 nm in (b) and 50 nm in (c).

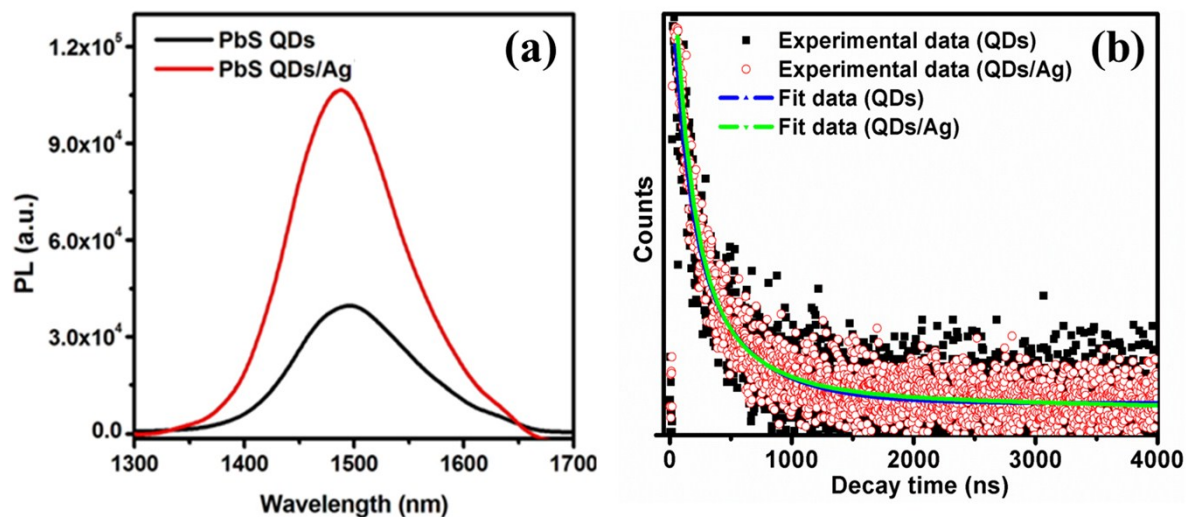


Fig. S3 Typical PL spectra (a) under 450 nm excitation and PL decay curves (b) under 444 nm excitation of PbS QDs with and without the presence of Ag#1.

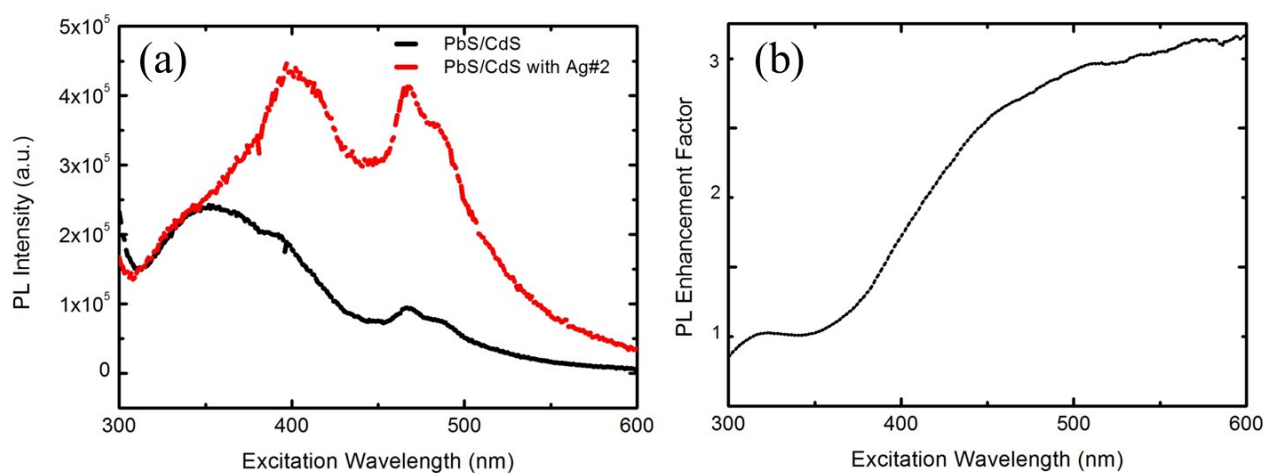


Fig. S4 (a) PL intensity at the emission peak wavelength of 1190 nm of PbS/CdS QDs with and without the presence of Ag#2 as a function of excitation wavelength and (b) PL enhancement factor versus excitation wavelength.

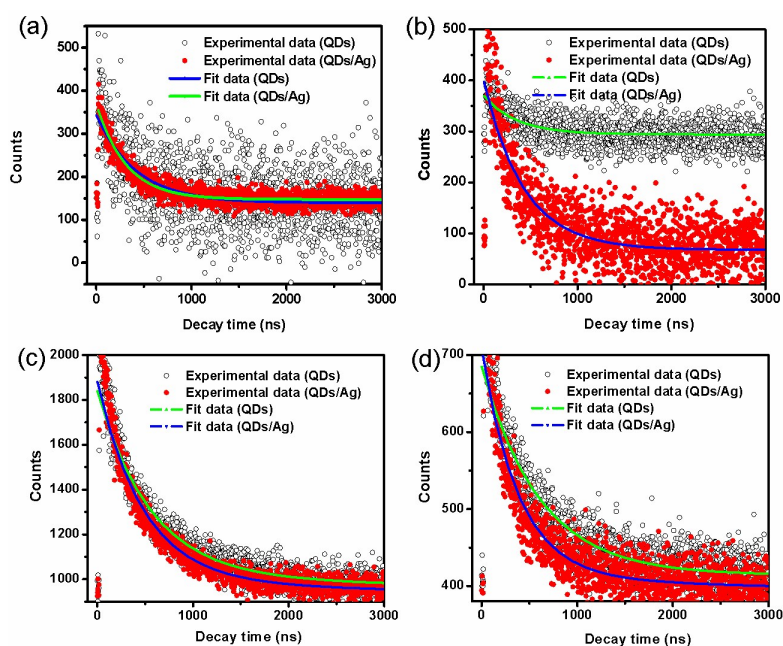


Fig. S5 PL decay curves for PbS/CdS QDs with and without Ag#2 measured at the emission peak of 1350 nm with 444 nm excitation (355 ± 15 ns versus 360 ± 20 ns) (a) and 636 nm excitation ($300 \text{ nm} \pm 15$ ns versus 360 ± 10 ns) (b), and at the emission peak of 1460 nm with 444 nm excitation (550 ± 30 ns versus 527 ± 8 ns) (c) and 636 nm excitation (462 ± 25 ns versus 529 ± 6 ns) (d) .

- 1 L. Cademartiri, J. Bertolotti, R. Sapienza, D.S. Wiersma, G. von Freymann and G.A. Ozin, *J. Phys. Chem. B*, 2006, **110**, 671.
- 2 H. Zhao, M. Chaker and D. Ma, *Journal of Physical Chemistry C*, 2009, **113**, 6497.
- 3 H. Zhao, M. Chaker, N. Wu and D. Ma, *Journal of Materials Chemistry*, 2011, **21**, 8898.
- 4 Q.A. Zhang, W.Y. Li, L.P. Wen, J.Y. Chen and Y.N. Xia, *Chemistry-a European Journal*, 2010, **16**, 10234.
- 5 H.L. Liang, W.Z. Wang, Y.Z. Huang, S.P. Zhang, H. Wei and H.X. Xu, *The Journal of Physical Chemistry C*, 2010, **114**, 7427.
- 6 H. Liang, H. Yang, W. Wang, J. Li, H. Xu, *Journal of the American Chemical Society*, 2009, **131**, 6068.
- 7 H.Y. Liang, H.G. Zhao, D. Rossouw, W.Z. Wang, H.X. Xu, G.A. Botton and D.L. Ma, *Chemistry of Materials*, 2012, **24**, 2339.