

Supporting Information

3D Assembly of Silica encapsulated Semiconductor Nanocrystals

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Experimental Section

Synthesis of CdSe/CdS core/shell QDs and CdSe/CdS/ZnS core/shell QDs

Highly fluorescent core/shell QDs were synthesized using a Hot-Injection procedure with subsequent SILAR coating reported previously.¹ The calculation of precursor injection amounts for the ZnS shells was done analogously to CdS shells.

Synthesis of In(Zn)P/GaP/ZnS core/shell QDs

The synthesis of In(Zn)P/GaP/ZnS was adopted from the literature.² In Brief, InZnP cores were synthesized by mixing In(OAc)₃ (0.12 mmol), Zn(OAc)₂ (0.06 mmol), Palmitic acid (0.36 mmol), and ODE (8 mL) in a 25 mL three neck round bottom flask. The solution was two times degassed in the vacuum and flushed with inert gas and then heated to 110 °C under vacuum for 30 min. After degassing, (TMS)₃P (0.06 mmol) in ODE (1 mL) were rapidly injected to the flask at 300 °C and held at 230 °C for 2 h. For the GaP shell coating, a precursor solution for GaP was prepared by mixing GaCl₃ (0.03 mmol) and oleic acid (0.1 mmol) in ODE (2 mL). This solution was added dropwise to the InZnP core solution at 200 °C. For the ZnS shell formation, Zn(OAc)₂ (0.3 mmol) was added to the reaction flask at room temperature and heated to 230 °C for 4 h. Finally, 1-dodecanethiol (0.5 mmol, 100 mg) was slowly injected into the flask and held for 2 h. The obtained multishell QDs were purified by 3 times precipitation with acetone/methanol and centrifugation and finally redispersed in toluene.

Synthesis of CdSeZnS alloy QDs

CdSeZnS QDs with chemical composition gradient were synthesized according to the literature.³ In brief, CdO (0.4 mmol), zinc acetate (4 mmol), oleic acid (17.6 mmol) and 20 mL of 1-octadecene were placed in a 100 mL round flask. The mixture was heated to 110 °C and degassed in the vacuum for 30 min, then filled with nitrogen and further heated to 310 °C to form a clear solution of Cd(OA)₂ and Zn(OA)₂. At this temperature, a mixture of Se powder (0.4 mmol) and S powder (4 mmol) dissolved in 3 mL of TOP were quickly injected into the reaction flask and the temperature of the reaction flask was set to 300 °C for promoting the growth of QDs. After 10 min of growth, the flask was cooled to room temperature to stop the growth. Finally, colloidal QD solutions in chloroform, hexane or toluene were obtained after 3 times purification by adding 20 mL of chloroform and an excess amount of acetone followed by centrifugation.

Synthesis of 5-(3-(trimethoxysilyl)propylaminomethyl)tetrazole

5-(3-(Trimethoxysilyl)propylaminomethyl)tetrazole [(MeO)₃Si-(CH₂)₃-NH-CH₂-CN₄H] was prepared by coupling (3-aminopropyl)trimethoxysilane (APTMS) to 5-chloromethyltetrazole (Cl-CH₂-CN₄H). Initial Cl-CH₂-CN₄H was prepared according to the literature.⁴ Anhydrous aluminium chloride (0.44 mol) was dissolved under stirring and cooling in 350 ml of anhydrous THF. Following this, sodium azide (1.20 mol) was added in small portions and the resulted mixture was heated to 55-60 °C for 2 h. After cooling to room temperature chloroacetonitrile (0.43 mol) was added in portions and the reaction mixture was refluxed for 24 h under stirring. Further, the mixture cooled to room temperature was poured into hydrochloric acid (15 %, 250 ml). Caution! The operation

should be carried out in a well-ventilated hood while excess of azide salt generates toxic hydrazoic acid. Finally, the solvent was evaporated at the rotary evaporator and the residue was recrystallized from diethyl ether-chloroform (1:4) yielding 5-chloromethyltetrazole as white crystals. For coupling of the tetrazole ligand to the silane, Cl-CH₂-CN₄H (0.004 mol), APTMS (0.004 mol), triethylamine (0.004 mol) and anhydrous THF (10 mL) were placed in a 50 mL three neck round bottom flask and flushed with inert gas for 15 min while stirring. Following this, the mixture was heated until boiling (60 to 70 °C) and kept stirring at that temperature under reflux for 6 h. Precipitate of triethylammonium hydrochloride formed was removed by filtration. The filtrate was then constrained until dryness on the rotary evaporator, resulting in a target tetrazole (MeO)₃Si-(CH₂)₃-NH-CH₂-CN₄ as a white solid.

Spectroscopical Data

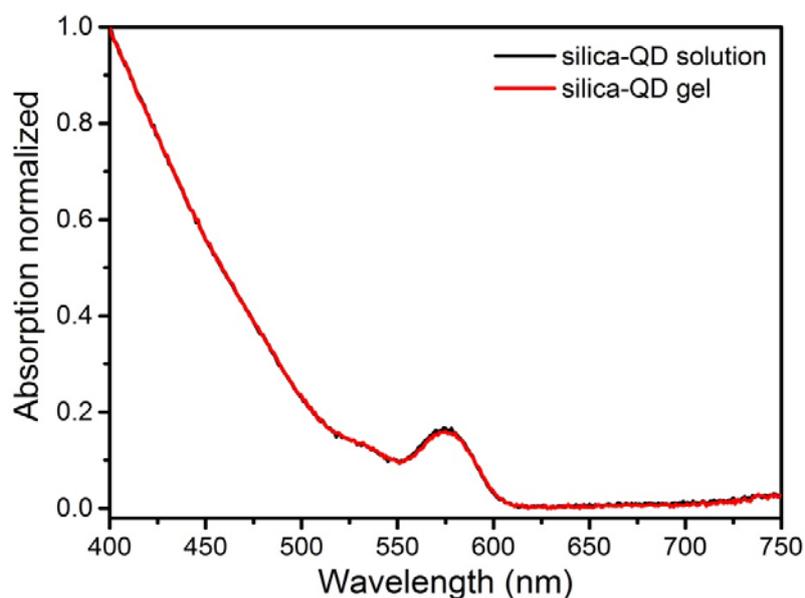


Figure S1: Absorption spectra of silica coated CdSe/CdS QDs as colloidal solution and hydrogel recorded using an integrating sphere setup. The absorption does not change upon gel formation

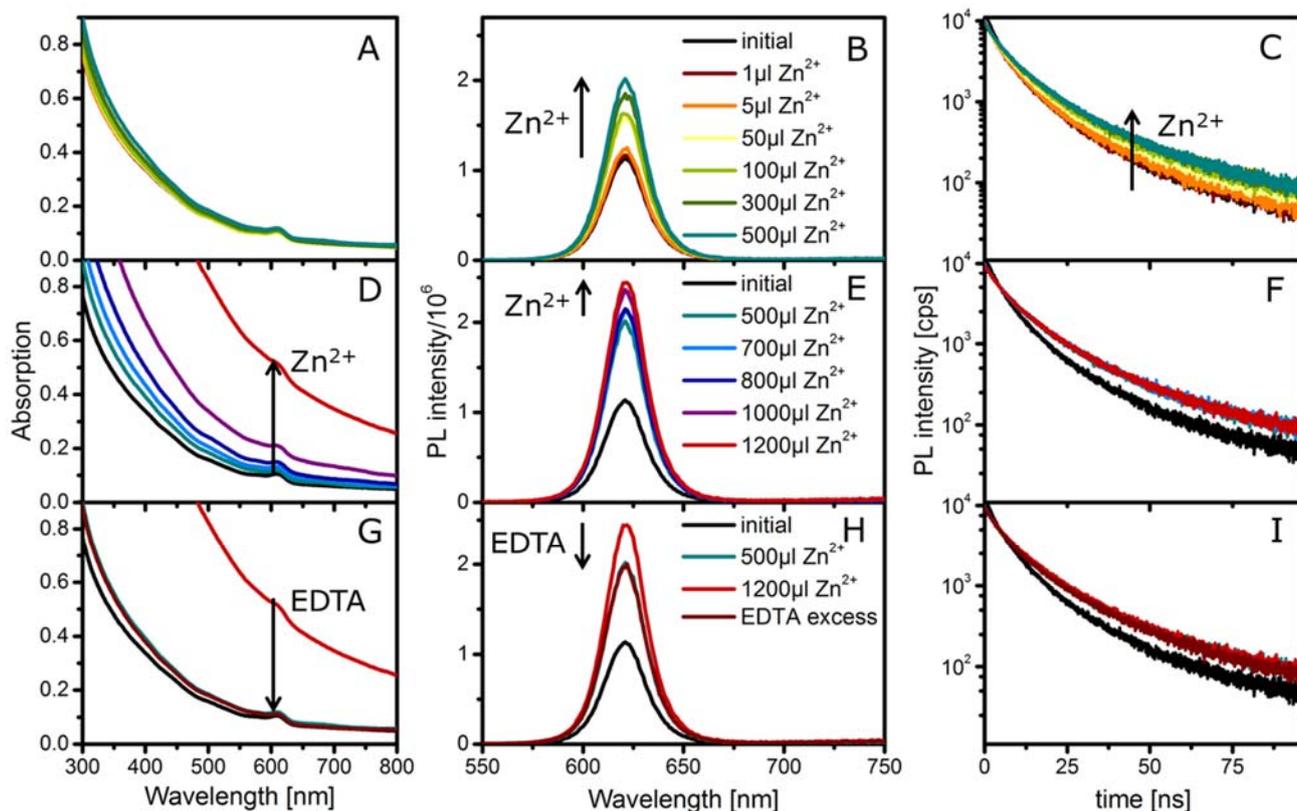


Figure S2: reversible gel formation with prior surface healing monitored by absorption and fluorescence spectroscopy. First additions of Zn^{2+} lead to a surface healing (the amounts of Zn^{2+} correspond to a 0.01 M solution). Absorption (A) remains unchanged but PL intensity (B) and PL lifetime (C) are enhanced. Further Zn^{2+} addition leads to gel formation, characterized by an increased absorption (D) due to increased scattering and an increased PL intensity (E). PL lifetime (F) does not change during gel formation. Dissolution of the gel is performed by the addition of an excess amount of EDTA. The gel is completely dissolved as can be seen from the corresponding absorption spectrum (G). The PL intensity (H) decreases to the state after surface healing, meaning that the PL intensity of the dissolved gel is higher than the initial solution. PL lifetime (I) also does not change during degelation and remains at the state after surface healing.

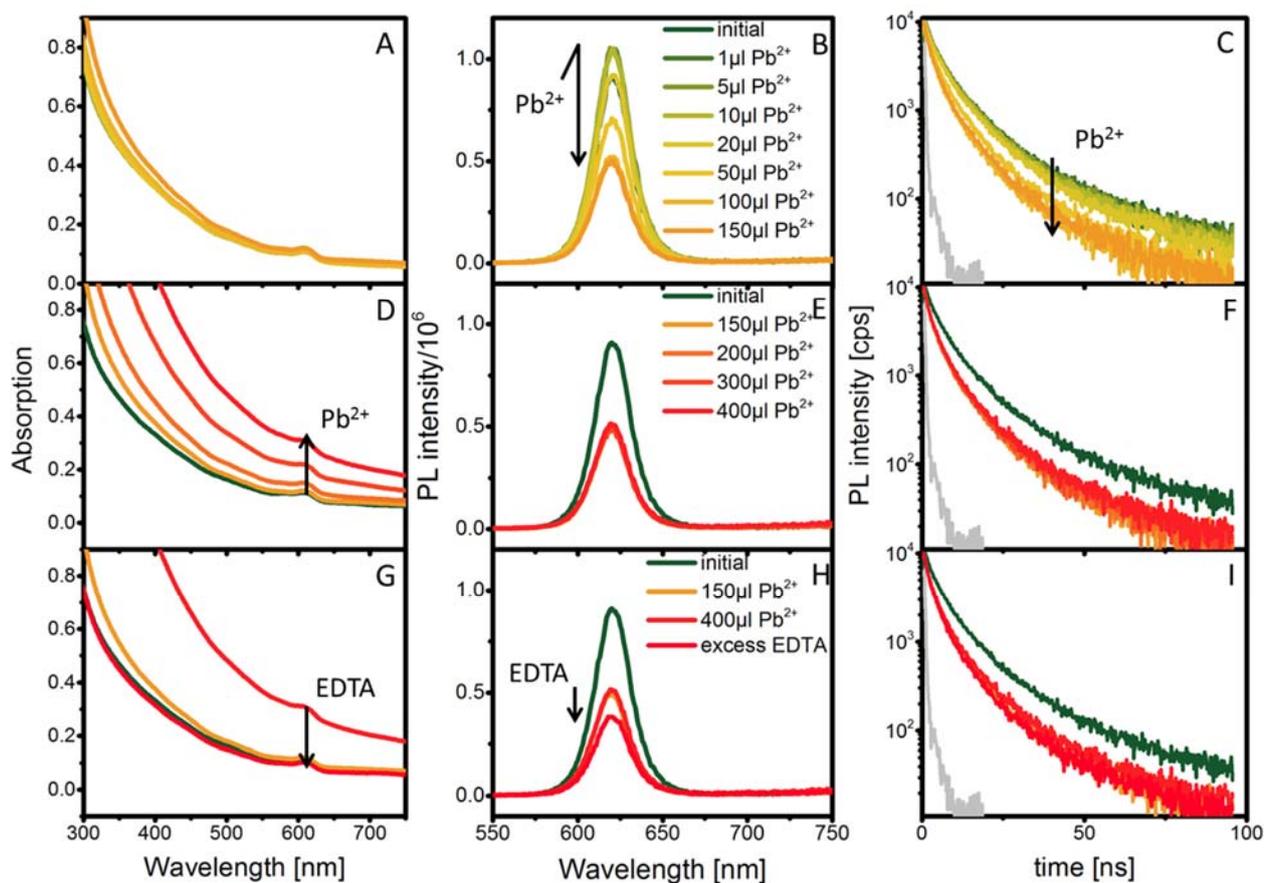


Figure S3: reversible gel formation with prior quenching monitored by absorption and fluorescence spectroscopy. First additions of Pb^{2+} lead to a quenching (the amounts of Pb^{2+} correspond to a 0.01 M solution). Absorption (A) remains unchanged but PL intensity (B) and PL lifetime (C) are decreased. Upon further Pb^{2+} addition, a gel is formed, characterized by an increased absorption (D) due to increased scattering and an increased PL intensity (E). PL lifetime (F) does not change during gel formation. Dissolution of the gel is performed by the addition of an excess amount of EDTA. The gel is completely dissolved as can be seen from the corresponding absorption spectrum (G). The PL intensity (H) further decreases, meaning that the PL intensity of the dissolved gel is much lower than the initial solution. PL lifetime (I) remains unchanged during degelation.

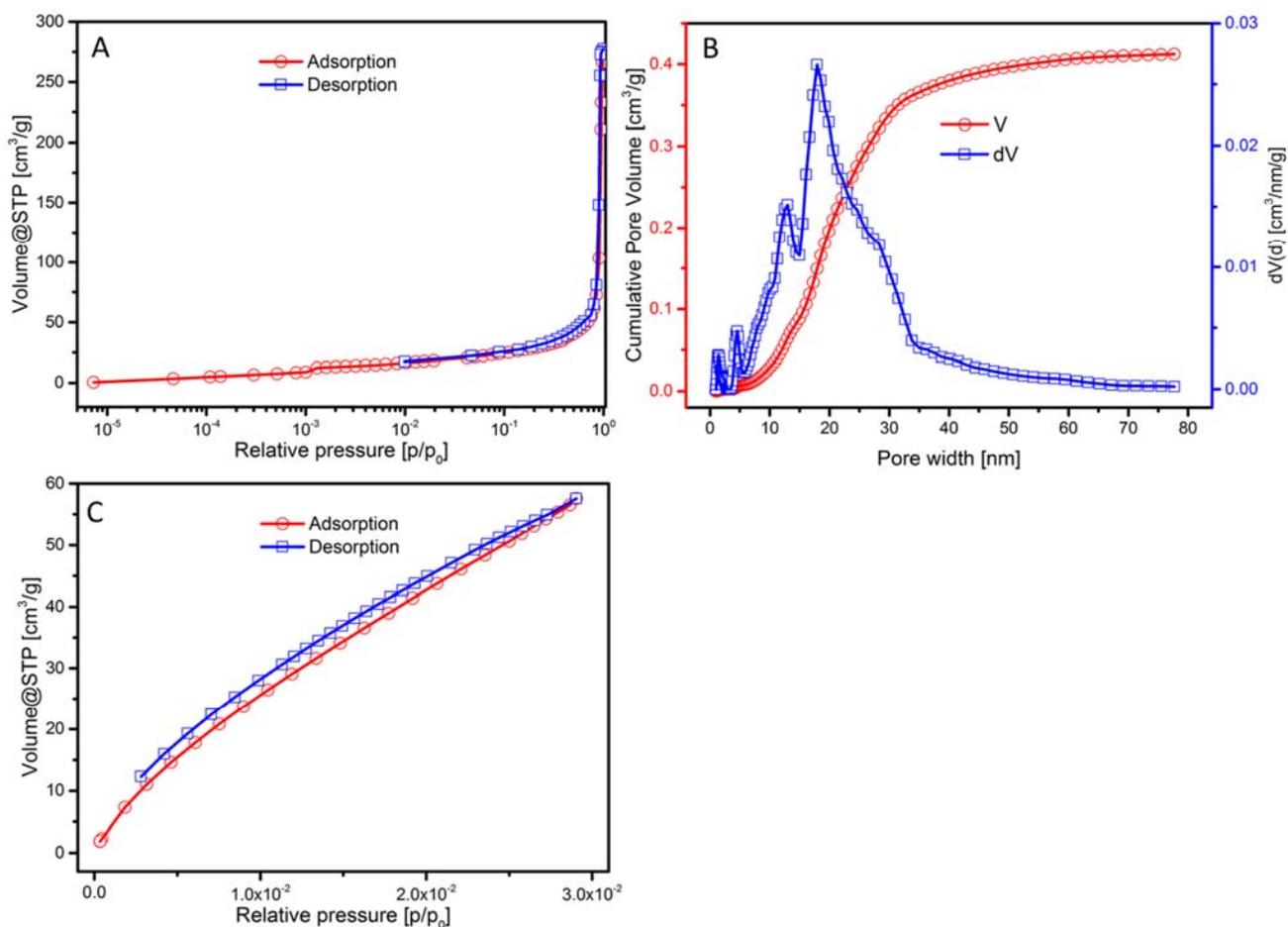


Figure S4: (A) logarithmic scaled nitrogen adsorption (at 77K) isotherm, (B) pore size distribution from NLDFT (cylindr. pores, adsorption branch) and (C) carbon dioxide adsorption (at 273.15 K) of microemulsion derived silica nanoparticles with average diameter of 42 nm.

References

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- (3) Bae, W. K.; Char, K.; Hur, H.; Lee, S.: Single-Step Synthesis of Quantum Dots with Chemical Composition Gradients. *Chemistry of Materials* **2008**, *20*, 531-539.
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