



# Self-assembly and photoluminescence evolution of hydrophilic and hydrophobic quantum dots in sol–gel processes



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## ABSTRACT

Highly luminescent quantum dots (QDs) with tunable photoluminescence (PL) wavelength were synthesized from several ligands to investigate the PL evolution in QD self-assembly via sol–gel processes. After ligand exchange, CdTe QDs were assembled into a chain by controlling the hydrolysis and condensation reaction of 3-mercaptopropyl-trimethoxysilane. The chain was then coated with a SiO<sub>2</sub> shell from tetraethyl orthosilicate (TEOS). Hollow spheres, fibers, and ring structures were created from CdSe/ZnS QDs via various sol–gel processes. CdTe QDs revealed red-shifted and narrowed PL spectrum after assembly compared with their initial one. In contrast, the red-shift of PL spectra of CdSe/ZnS QDs is small. By optimizing experimental conditions, SiO<sub>2</sub> spheres with multiple CdSe/ZnS QDs were fabricated using TEOS and MPS. The QDs in these SiO<sub>2</sub> spheres retained their initial PL properties. This result is useful for application because of their high stability and high PL efficiency of 33%.

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## 1. Introduction

Self-assembly refers to a process by which disordered parts, for example, molecules and small particles build an ordered structure via various local specific interactions. Such “bottom-up” methodology consists of inorganic/organic hybrid systems in which the nanoparticles assemble or co-assemble into superlattices [1]. Metallic and semiconductor nanoparticles can be exploited as building blocks for use in sensing and optical applications as well as for designing photonic, electronic, and magnetic devices. Because electronic and optical properties of quantum dots (QDs) with nanoscopic dimensions are often altered by the effects of quantum confinement imposed upon excitons, the self-assembly of quantum dots (QDs) has gained much attention. The self-assembly of anisotropic QDs has shown great promise for applications in areas such as optics, electronics, catalysis, magnetic storage, and biological labeling and sensing because of their high stability compared with initial QDs. For example, the optoelectronic applications of QDs generally require either large-area deposition of a large number of QDs (as in light-emitting diodes and solar cells) or using a small number of QDs as building blocks

for more complex structures [2–6]. Control over the self-assembly of QDs has great importance for further applications.

The self-assembly of nanoparticles normally occur either through direct interactions (e.g., by interparticle forces), or indirectly using a template or an external field [7]. Several techniques have been employed for the self-assembly of nanoparticles [8]. Typically, various templates such as, soft matter, and even organic monolayers in regular arrays on solid substrates. Another recent development has involved the use of capillary lithography to direct metal and semiconductor nanoparticles to specific locations in groves and wells [9,10]. As for the self-assembly of semiconductor QDs, several methods have been developed to arrange QDs in complex, ordered networks. For example, Yakes et al. have demonstrated techniques for growing three-dimensional (3D) QD configurations using molecular beam epitaxy on faceted template islands [11]. Chen et al. reported on the controlled formation of two-dimensional (2D) periodic arrays of ring-shaped nanostructures assembled from CdSe semiconductor QDs [8]. To take full advantage of the potential of self-assembled QDs, applications require regular assembly of QDs, especially, to assemble QDs into various freestanding structures. Although the assembly of the QDs has received much attention, the mechanism of their formation remains poorly understood.

To date, the self-assembly fabrication methods have shown great potentiality for directing the organization of QDs.

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For example, Chen et al. reported on the controlled formation of 2D periodic arrays of ring-shaped nanostructures assembled from CdSe QDs by using an evaporative templating method [8]. The 2D self-assembly of CdSe QDs was fabricated at the air–water interface [11]. The formation of these assemblies, however, is presently limited by a lack of convenient, inexpensive, and rapid templating methods. This problem has motivated considerable efforts to develop improved patterning techniques. Organosilane has been known for its layered but amorphous construction during assembly [12,13]. After hydrolysis and condensation, the 1D–3D networks of SiO<sub>2</sub> are created. Thus, the self-assembly of QDs may occur via the condensation. The main contributor to the assembly was from a continuous 2D or 3D network of (SiO–O–SiO)<sub>n</sub> rather than a simple 1D connection ((Si–O–Si)<sub>n</sub>) [7]. Advantages of this assembly technique include high stability, biocompatibility, establishing limiting QD area, easy manipulation, and high PL properties. The latter is of great significance because much of the attention in QDs has been focused on their unique optical properties for applications. However, the study on QD assembly from silica networks is limited by their complex hydrolysis and condensation reactions. Very little literature focused on such assembly.

In this paper, we demonstrate sol–gel techniques to create a variety of 1D–3D assemblies of QDs through the controlling of hydrolysis and condensation reactions of silane agents. Aqueous CdTe QDs were assembled into a chain with narrowed and red-shifted PL spectrum and decreased PL efficiency. Large hydrophobic CdSe/ZnS QDs with a PL peak wavelength of 655 nm were assembled into hollow spheres and 2D fibers through sol–gel processes at room temperature and a reflux route, respectively. In contrast, small CdSe/ZnS QDs with a PL peak wavelength of 585 nm were assembled into a ring-morphology. These CdSe/ZnS QDs revealed small red-shifted PL spectra. Furthermore, HDA-capped CdSe/ZnS QDs in the assembly (SiO<sub>2</sub> sphere) retained their initial PL properties including PL peak wavelength, full width at half maximum (FWHM) of PL spectra, and PL efficiency. These assemblies may be utilized for further applications because of their high PL properties.

## 2. Experimental

### 2.1. Chemicals and materials

All chemicals were of analytical grade or of the highest purity available, and, unless otherwise indicated, were obtained from Sigma–Aldrich and used as received. Tetraethyl orthosilicate (TEOS) Cadmium chloride (CdCl<sub>2</sub>·2.5H<sub>2</sub>O) (99%), zinc acetate (Zn (Ac)<sub>2</sub>, 99.99%), tellurium powder (Te, 99%), TGA (90%), and NaBH<sub>4</sub> (≥96%) were taken from Shanghai Guoyao Chemical Reagent Company. Selenium powder (Se, 99.99%) was purchased from Shanghai Meixing Chemical Reagent Company. An ammonia solution (NH<sub>3</sub>·H<sub>2</sub>O) (25% wt) was supplied by Laiyangkangde Chemical Reagent Company. Sodium Selenite (Na<sub>2</sub>SeO<sub>3</sub>, 97%) was supplied by Tianjin Guangfu Chemical Reagent Company. Milli-Q water ( $\rho \sim 18 \text{ M}\Omega \text{ cm}$ ) was used as a solvent.

### 2.2. Preparation of QDs

TGA-capped CdTe QDs (Sample QD 1) in an aqueous solution were prepared using a procedure that includes using cadmium perchlorate and hydrogen telluride, as described elsewhere [14]. Typical, NaBH<sub>4</sub> was first mixed with Te in water with a molar ratio of 5/1 for NaBH<sub>4</sub>/Te to obtain a fresh sodium hydrogen telluride (NaHTe) solution at 60 °C. TGA-capped CdTe QDs were fabricated from CdCl<sub>2</sub> of 0.4 mmol and TGA of 0.6 mmol mixed in 25 mL of water to get a precursor solution followed by adjusting the pH

value up to 10 using a NaOH solution of 1 M. After bubbled by N<sub>2</sub> for 30 min, the fresh NaHTe solution was added under continuous stirring. The typical molar ratio of Cd/Te/TGA was 1/0.5/1.5. The mixture was subsequently refluxed for 10 h.

CdSe cores were prepared by a hot injection approach [15]. Typically, 0.1 mmol of CdO and 0.4 mmol of stearic acid were loaded into a four neck flask and heated to 150 °C under N<sub>2</sub> flow till CdO dissolved completely. Hexadecylamine of 1.94 g was added to the flask, and the mixture was heated to 300 °C under N<sub>2</sub> flow to form an optically clear solution. The trioctylphosphine (TOP) Se solution with 1 mmol of Se, 1 mmol of TOP, and 2 g of 1-octadecene (ODE) were swiftly injected into the reaction flask with stirring. The temperature was set at 300 °C for the growth of the CdSe cores. To control the sizes of CdSe cores, reaction time was adjusted. CdSe/ZnS core/shell QDs (Samples QD 2 and QD 3) were prepared using a similar procedure with CdSe cores. Trioctylphosphine oxide (TOPO) and HDA were mixed as ligands. Typically, 2 mL of ODE, 2 g of TOPO, 1 g of HDA, and 0.05 mmol of Zn(Ac)<sub>2</sub> were added in a four neck round bottom flask with stirring under N<sub>2</sub> flow up to 300 °C. 0.1 mmol of powder sulfur was dissolved in 0.5 mL of TOP and subsequently mixed with 2 mL of TOP to prepare a clear solution (TOPS solution). 1 mL of CdSe core solution with a QD concentration of  $1 \times 10^{-4} \text{ M}$  was added in the flask with vigorous stirring. The solution was heat treated up to 300 °C. 2.5 mL of TOPS solution was injected into high temperature mixture. The resulting solution was cooled down to room temperature. The QDs were precipitated by adding methanol into the hexane solution and isolated by decantation using a separating funnel. The samples were dispersed in hexane for further characteristics. For comparison, we prepared CdSe/ZnS QDs by coating with a ZnS shell just by using HDA as a ligand (Sample QD 4).

### 2.3. Self-assembly of QDs

Table 1 summarizes the preparation conditions of assembled samples. CdTe QDs were assembled via a ligand exchange and SiO<sub>2</sub> coating procedure. Firstly, 2-propanol was added to precipitate CdTe QDs. The QDs were then re-dispersed in water with NaOH to adjust the pH up to 9. This solution was added to the methanol solution of MPS with stirring for 5 h. The volume ratio of H<sub>2</sub>O/ethanol was typically 1/5. TEOS and ammonia were added to create the outer SiO<sub>2</sub> shell. TEOS and diluted ammonia were added gradually to control the number of SiO<sub>2</sub> monomers in the solution. The final volume ratio of TEOS/H<sub>2</sub>O was 0.008. The total reaction time from TEOS addition to completion was 5 h. Samples were centrifuged, washed, and re-dispersed in water to obtain Sample 1 for further characterization. To control the morphology of assemblies, the self-assembly of hydrophobic CdSe/ZnS QDs were carried out via several sol–gel processes. For the QDs with a long PL peak wavelength of 655 nm, a sol–gel process at room temperature was used to create hollow spheres via a silanization of the QDs and subsequent the hydrolysis and condensation of TEOS. The QDs in toluene solution were firstly precipitated using a mixture of methanol and 2-propanol with a volume ratio of 3–1. The QDs were then re-dispersed in toluene solution. 0.2  $\mu\text{L}$  of TEOS was added in

**Table 1**  
Preparation conditions and properties of assembled samples.

Sample	QDs	Silane agent	Temperature (°C)	Solvent
1	QD 1	MPS, TEOS	RT <sup>a</sup>	Ethanol
2	QD 2	TEOS	RT	Toluene in ethanol
3	QD 2	TEOS	100	Toluene in ethanol
4	QD 3	MPS	RT	Water
5	QD 4	TEOS, MPS	RT	Water

<sup>a</sup> RT – room temperature.

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