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## Full Length Article

## Thermal stabilities of cadmium selenide and cadmium-free quantum dots in quantum dot–silicone nanocomposites

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## ABSTRACT

To investigate the thermal stabilities of CdSe and Cd-free quantum dots (QDs) in QD–silicone polymer nanocomposites, we synthesized both CdSe and CuInS<sub>2</sub> (CIS) QDs capped with different surface ligands (oleic acid (OA) and 1-dodecanethiol (1-DDT)). A comparison of the quantum yields of dried QDs after exposure to different temperatures revealed that the CIS QDs and 1-DDT ligands exhibited higher thermal stabilities than the CdSe QDs and OA ligands, respectively. We also prepared QD–silicone nanocomposites containing different types of QDs by varying the curing temperature and time and observed that nanocomposites containing CdSe QDs exhibited discoloration at high temperatures, whereas those containing CIS QDs did not. Moreover, the highest quantum efficiency (QE) of the QD–silicone nanocomposites was observed in the case of CIS QDs capped with 1-DDT and the lowest was observed in the case of CdSe QDs capped with OA. Because the dispersion states of QDs were not substantially affected at high temperatures, we attributed the high QE of nanocomposites containing the CIS QDs capped with 1-DDT to the superior thermal stability of CIS QDs and their surface ligand (i.e., 1-DDT).

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## 1. Introduction

Semiconductor nanocrystals, which are often referred to as quantum dots (QDs), exhibit interesting optical properties such as a broad excitation wavelength, narrow emission band, size-dependent emission wavelength, and resistance to photobleaching [1,2]. Because of these characteristics, QDs have been extensively studied for various potential applications, including optoelectronic devices, renewable energy, bioimaging, and sensors [3–7]. In particular, QDs are promising alternatives to phosphors in the development of light-emitting diodes (LEDs). In contrast to conventional Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce<sup>3+</sup> (YAG:Ce) phosphors, QDs exhibit low light scattering, narrow emission band, high photoluminescence quantum yield (PLQY), and high photostability, enabling high color accuracy and efficiency of QD-based LEDs. Therefore, many attempts have been made to fabricate QD-based LEDs for next-generation LEDs [8,9].

When QDs are used in LED applications, they are usually embedded in packaging materials for protection against the environment [10]. For LED packaging materials, silicone-based polymers are widely used because they exhibit high thermal stability, mechanical strength, transparency, and stability against discoloration. Although QDs are embedded in a polymer matrix, nanosized QDs still suffer from

surface defects and interparticle aggregation when they are exposed to severe conditions, which reduces the luminescence efficiency of LED devices [11]. To date, various approaches such as the use of hybrid particles and surface modification of QDs and polymer matrices have been used to improve the dispersion state of QDs and hence to enhance the photoluminescence (PL) properties of resulting QD–polymer nanocomposites in LED applications [12–14].

Until recently, most studies have focused on Cd-based QDs such as CdSe or CdTe because they exhibit high PLQYs and their emission wavelength is easily tunable over an entire visible spectral region. However, because of a recent regulation of toxic heavy metals by the restriction of the use of certain hazardous substances (RoHS) directive, heavy-metal-free QDs have been studied as alternatives. Moreover, the PL properties (i.e., luminescence intensity and lifetime) of CdSe QDs are known to irreversibly deteriorate with increasing temperature [15]. This deterioration suggests that the thermal instability of CdSe QDs can also lead to the degradation of the PL properties in QD-embedded polymer nanocomposites. However, to the best of our knowledge, few studies are available on the thermal stability of Cd-free QDs. In this paper, we investigate the thermal stabilities of QDs and QD-embedded polymer nanocomposites using both CdSe and Cd-free CuInS<sub>2</sub> (CIS) QDs capped with different surface ligands (oleic acid and 1-dodecanethiol). The knowledge gained from this study is expected to provide a design protocol for both QDs and QD-embedded polymer nanocomposites that maximize PL characteristics even at high temperatures.

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## 2. Materials and methods

### 2.1. Materials

Copper(I) iodide (CuI, >99.5%), indium(III) acetate (In(Ac)<sub>3</sub>, >99.99%), 1-dodecanethiol (1-DDT, >98%), oleic acid (OA, >90%), 1-octadecene (1-ODE, >90%), zinc acetate (Zn(Ac)<sub>2</sub>, >99.99%), zinc stearate (technical grade), selenium (Se) powder (>99.5%), trioctylphosphine (TOP, >97%), cadmium oxide (CdO, >99.99%), and sulfur (S) powder (>99.98%) were purchased from Sigma-Aldrich. All chemicals were used without further purification.

### 2.2. Synthesis of CdSe/ZnS QDs

CdSe/ZnS core/shell QDs with a chemical composition gradient were synthesized using a previously reported method [16]. Briefly, 0.8 mmol of CdO, 16 mmol of Zn(Ac)<sub>2</sub>, 16 mL of OA, and 60 mL of 1-ODE were mixed in a 250-mL flask with magnetic stirring, and the reactor was degassed for 30 min at 130 °C. The reactor was then heated to 300 °C under a N<sub>2</sub> atmosphere, during which the reaction mixture became transparent. A stock solution was separately prepared by mixing 16 mmol of S powder, 0.8 mmol of Se powder, and 8 mL of TOP in a glass vial with magnetic stirring. The stock solution was then quickly injected into the reaction mixture, and the temperature was maintained at 300 °C for 10 min for QD growth. The resulting QDs were purified by adding chloroform and an excess amount of acetone, followed by centrifugation at 7000 rpm for 15 min. This purification step was repeated three times, and the QDs were redispersed in chloroform for further use.

To test the thermal stability of surface ligands, OA ligands on the surface of OA-capped CdSe QDs were exchanged with 1-DDT ligands as follows. OA-capped CdSe QDs were dispersed in 10 mL of chloroform in a 100-mL three-neck flask, and 15 mL of 1-DDT and 10 mL of 1-ODE were added. The mixture was mixed with magnetic stirring and N<sub>2</sub> purging and was allowed to react for 12 h at 120 °C. The mixture was then cooled to room temperature, and the resulting QDs were purified by the method described above.

### 2.3. Synthesis of CIS/ZnS/ZnS QDs

A previously reported method [17] with modifications was used to prepare Cd-free core/double-shell (CIS/ZnS/ZnS) QDs. Briefly, 0.4 mmol of CuI, 1.5 mmol of In(Ac)<sub>3</sub>, and 15 mL of 1-DDT were mixed in a 250-mL flask with magnetic stirring, and the mixture was degassed at 130 °C for 30 min. The mixture was then heated to 230 °C within 210 s under N<sub>2</sub> purging. The color of the mixture became light orange at ~170 °C and then dark red when the temperature reached 230 °C. After the synthesis of the CIS core was completed, the core was coated with ZnS double shells to increase the QY. For the first shell, we prepared a Zn stock solution by mixing 12 mL of 1-ODE, 4 mL of OA, 3 mL of 1-DDT, and 12 mmol of Zn(Ac)<sub>2</sub> with magnetic stirring for 15 min at 190 °C. This stock solution was added dropwise to the CIS core suspension over a period of 180 s, followed by reaction at 240 °C for 60 min to produce CIS/ZnS core/shell QDs. For the second shell, another stock solution was prepared by mixing 12 mL of 1-ODE, 3 mL of 1-DDT, and 3.0 mmol of Zn(Ac)<sub>2</sub> at 130 °C for 15 min. The second stock solution was added dropwise to the CIS/ZnS core/shell QD suspension over a period of 180 s, followed by the second shell formation at 240 °C at 60 min. The resulting QDs were purified using the method described above.

### 2.4. Fabrication of QD–silicone nanocomposites and thermal stability experiments

Sylgard-184 (Dow Corning) was used to fabricate QD–silicone nanocomposites. We mixed 2.42 g of Sylgard 184 prepolymer, 0.242 g

of cross-linker, and 0.824 g of the QD suspension (10 wt%) for 3 min using a vortex mixer. The mixture was placed in a vacuum oven for 1 h at room temperature to remove the solvent and air bubbles. The final concentration of QDs in the polymer nanocomposite was 3 wt%. The prepared nanocomposite was then cured in the convection oven at various temperatures and curing times to investigate its thermal stability.

### 2.5. Characterization

We used PL (PerkinElmer, LS55) spectroscopy and UV–vis (Shimadzu, UV-1650PC) spectroscopy to acquire emission and absorption spectra, respectively. Through high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100, 200 kV), we observed the morphology of the QDs. We performed proton nuclear magnetic resonance (<sup>1</sup>H NMR) experiments using a Bruker Advance II (400 MHz) spectrometer to characterize surface ligands on the QDs. In the NMR experiments, we used CDCl<sub>3</sub> containing 0.3 v/v% of tetramethylsilane as the solvent. We estimated the quantum yield of QD suspensions by a relative method using rhodamine 6G as a standard dye (QY=95% in ethanol) [18]. Moreover, we estimated the quantum efficiency (QE) of the QD–silicone nanocomposites using an integrating sphere with a 460-nm excitation wavelength (Otsuka Electronics, QE-1000). We observed the dispersion state of the QDs in the nanocomposites using confocal laser microscopy (Olympus, Fluoview FV 1000).

## 3. Results and discussion

### 3.1. Characterization of as-synthesized QDs

Two types of QDs, i.e., CdSe and Cd-free CIS QDs, were synthesized by previously reported methods [16,17]. Fig. 1 shows a HR-TEM image and the UV–vis absorption and emission spectra of the synthesized CdSe/ZnS core/shell QDs. On the basis of the HR-TEM image shown in Fig. 1(A), the average diameter of the CdSe/ZnS QDs was estimated to be ~9 nm. The emission spectrum shown in Fig. 1(B) indicates a peak at 523 nm with a full width at half maximum (FWHM) of 40 nm corresponding to a green emission (inset). Using rhodamine 6G as a standard, the QY of the CdSe/ZnS QDs was determined to be 0.71, which is comparable to the QY previously reported for these QDs.

In the synthesis of Cd-free CIS QDs, ZnS double shells were grown onto the CIS core to improve the QY of the CIS core, which was only ~0.04. The XRD pattern of the CIS core shown in Fig. 2(A) reveals three distinct reflection peaks at  $2\theta=28.3^\circ$ ,  $47.2^\circ$ , and  $55^\circ$  corresponding to the tetragonal chalcopyrite structure [19]. As the ZnS shell formed on the CIS core, these peaks shifted to larger  $2\theta$ , approaching the (111), (220), and (311) planes of the zinc blende ZnS phase. Using the Debye–Scherrer formula, the average diameter of the CIS/ZnS QDs was estimated to be ~2.7 nm. The TEM image shown in Fig. 2(B) reveals that the average diameter of the CIS/ZnS QDs was ~3 nm, consistent with the XRD results. The emission spectrum shown in Fig. 2(C) reveals a peak at 561 nm with an FWHM of 105 nm, corresponding to a yellow emission (see inset). Moreover, the QY of the CIS/ZnS double-shell QDs was ~0.6, which is a 15-fold increase from that of the CIS core.

### 3.2. Thermal stabilities of dried QDs capped with different surface ligands

One of the most important characteristics of QDs in LED applications is thermal stability because they are required to withstand high temperatures during LED operation. To test the long-term thermal stability of the synthesized QDs, we exposed dried QDs at temperatures between 70 °C and 170 °C for 12 h and determined their QYs.

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