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Synthesis of CdSe/ZnSe quantum dots passivated with a polymer for oxidation prevention

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ABSTRACT

Surface overcoated CdSe/ZnSe core/shell structured quantum dots (QDs) with enhanced stability, narrow size distribution and strong photoluminescence have been successfully synthesized by using a simple poly(methylmethacrylate) (PMMA) coating on nanoparticles. When applied to the surface of QDs, the polymer coating provided ultra-dispersion stability and a high fluorescence quantum yield of above 80% that prevented chemical degradation, such as aggregation and Ostwald ripening. The degree of degradation was measured with respect to storage time (1, 7, 15, and 30 days) in order to provide a comparison between PMMA uncoated and coated QDs, and the oxidation of QDs was confirmed with Fourier transform infrared spectroscopy.

1. Introduction

Semiconductor quantum dots (QDs) are a special class of intermediate nanocrystals between a few hundred and thousand atoms in size [1]. When the characteristic dimension of the nanocrystals is sufficiently small, the quantum confinement effect leads to an increasing band gap as the nanostructure size decreases [2]. Consequently, light absorption and emission ranges from ultraviolet to near-infrared can be realized by controlling the mean size of the QDs [3]. Consequently, light absorption and emission ranged from ultraviolet to near-infrared through a control of the mean size of the QDs [2,4–6]. While the most generally synthesized QDs are of the cadmium chalcogenide group (CdSe, CdTe, and CdS) for the ease of synthesis and handling [7], cadmium selenide (CdSe) has been used because of its highly luminescent nanoparticles of the visible region [8]. The core–shell structured quantum dot, which is overcoated nanocrystallites with several wider band gap inorganic materials (ZnS, ZnSe, and CdS), can improve fluorescence quantum yields by confining both electrons and holes in the core [9]. The use of such heterostructures (core–shell QDs) exhibits greater tolerance to the processing conditions necessary for incorporation into solid state structures [7]. In addition, it is clear that the CdSe/ZnSe core/shell structure QDs assure better photoluminescence (PL) QYs, because the lattice parameter between the CdSe core and ZnSe shell materials is smaller than the other shell inorganic materials. The large lattice mismatch of the core–shell QDs yields the formation of structural defects at the core/shell interface, resulting in fluorescence quenching [10].

Surface overcoating has not been performed to obtain optical properties and intense PL. The exposure of the QD surface to the surrounding medium, e.g. oxygen or humidity in air, leads to aggregation and Ostwald ripening under ambient conditions [11]. As a result, the stability of fluorescence QY and dispersion is reduced.

In this study, a CdSe core and CdSe/ZnSe core/shell structured QDs were synthesized utilizing a micro-reactor. Furthermore, to enhance the stability of nanoparticles against aggregation and Ostwald ripening, surface overcoating with poly(methylmethacrylate) (PMMA) was used on the CdSe core and CdSe/ZnSe core/shell. Polymer-stabilized QDs were obtained that possessed steric stabilization, thereby eliminating the susceptibility to environmental factors [12,13]. Many groups have studied the QD/PMMA nanocomposites for protecting the surface oxidation of QDs in the environmental conditions using the polymerization of MMA monomer [14–16]. However, the PMMA coating with polymerization is complicated and less compatible method due to selective polymerization. Our process for PMMA coating is very simple, and can be used to passivate on the surface of various QDs. The QD samples were systematically exposed in ambient conditions for several days (1, 7, 15, and 30 days), and measured with UV–vis and photoluminescence spectroscopy in order to draw a comparison between PMMA uncoated and coated QDs.

2. Experimental details

CdSe core and CdSe/ZnSe core/shell QDs were synthesized by a previously reported process [10]. Cadmium acetate dihydrate ($Cd(OAc)_3 \cdot 2H_2O$) and oleic acid were dissolved in 1-octadecene (ODE) at 180 °C under the flow of argon. Se powder was dissolved in trioctylphosphine (TOP) at

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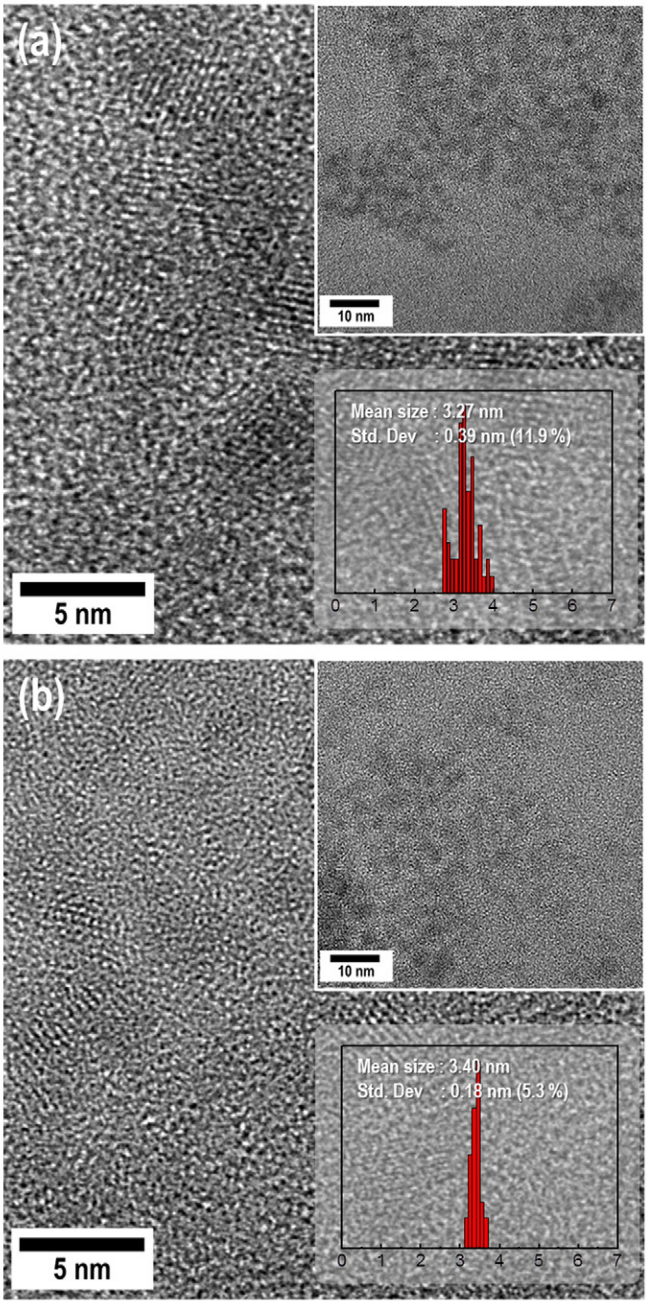

Fig. 1. The (a) low and high resolution TEM images, and size distribution of CdSe core QDs, and (b) low and high resolution TEM images, and the size distribution of CdSe/ZnSe core/shell QDs.

room temperature. CdSe core QDs were obtained by heating the raw material solutions in a micro-reactor heated at 230 °C for 20 s. The heating time was controlled using a common syringe pump.

To prepare the ZnSe raw material, Zinc acetate dihydrate ($Zn(OAc)_3 \cdot 2H_2O$) and oleylamine were dissolved in ODE at 180 °C. For the CdSe/ZnSe core/shell QDs, the raw material was mixed with the CdSe core solution. CdSe/ZnSe QDs were obtained after a reaction in the micro-reactor at 200 °C for 90 s. After washing the CdSe/ZnSe QDs, the particles were redispersed in chlorobenzene. For the synthesis of PMMA-coated CdSe/ZnSe QDs, PMMA was added to the stirred solution (20% wt/wt).

UV–visible absorption spectra (UV–vis, Optizen 2020UV, Mecasys) and photoluminescence emission spectra (PL, CUBE 405 nm, 100 mW, COHERENT) were used to determine the absorption and emission spectra. To analyze the size and distribution of the resulting nanoparticles, the prepared CdSe core, and CdSe/ZnSe core/shell QDs were characterized by transmission electron microscopy (TEM, JEM-2100F, JEOL). The dispersion stability of QDs was measured by multiple light scattering (Turbiscan-Lab, Formulation) in a vial, which was examined every 6 h over the course of 7 days. Lastly, to compare the samples just after synthesis and after 30 days, Fourier transform infrared spectroscopy (FT-IR, Avatar 360 E.S.P, Nicoltet) was used.

3. Results and discussion

CdSe core QDs with a reaction time of 20 s and CdSe/ZnSe core/shell QDs were synthesized utilizing a micro-reactor. Fig. 1 shows high resolution transmittance electron microscopy (HR-TEM) images of the prepared QD samples. The CdSe core and CdSe/ZnSe core/shell QDs were 3.27 nm (±0.39 nm) and 3.40 nm (±0.18 nm) in diameter, respectively, thus it is evident that the micro-reactor can synthesize highly uniform QDs. In previous research, the micro-reactor has been demonstrated to be a powerful technology with precise control of heat transfer and can provide high mix and low volume production in comparison with general batch methods [17]. Additionally, the size distribution of CdSe/ZnSe core/shell QDs was narrower than the CdSe core. These results can be explained by the Ostwald ripening, that smaller particles dissolve in the solution and then are deposited onto the surface of the larger particle in order to reduce the surface energy.

PMMA-coated CdSe/ZnSe composite QDs were prepared by a simple coating on the surface of the CdSe/ZnSe core/shell QDs for enhancing the dispersion and fluorescence stability. The change in transmittance versus time, which served as an investigation of aggregation kinetics, was successfully studied using a recently developed optical analyzer (Turbiscan). The main advantage of Turbiscan is to observe the disperse stability with greater accuracy than just the operator's naked eye. Using this measurement, the destabilization phenomena, such as particle migration (creaming, sedimentation) and aggregation (coalescence, flocculation), readily detect concentrated or opaqure emulsions or suspensions. The disperse stability was measured by detecting variations in the concentration of the solution using the whole height of the sample [18,19]. As seen in Fig. 2, CdSe core and CdSe/ZnSe core/shell QDs dispersed in hexane continually increased over the course of 7 days, due to agglomeration (such as 'arms' or 'branches') of CdSe core and CdSe/ZnSe core/shell QDs. However, the transmission flux of PMMA-coated CdSe/ZnSe composite QDs (Fig. 2(c)) slightly increased by 0.5%. It was thought that the PMMA polymer not only provided steric stabilization of the nanoparticles but was less susceptible to ambient conditions such as humidity or oxygen. The quantum yield, which is

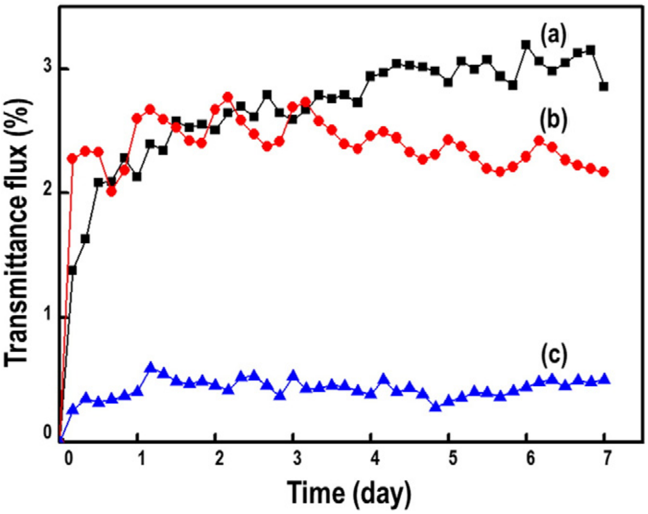

Fig. 2. Dispersion stability of (a) CdSe core, (b) CdSe/ZnSe core/shell and (c) PMMA-coated CdSe/ZnSe QDs measured every 6 h.