Chemical Engineering Journal 324 (2017) 19–25

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

All-quantum-dot emission tuning and multicolored optical films using layer-by-layer assembly method

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HIGHLIGHTS

- A novel all-quantum-dot multilayer photoluminescent film (PLF) was fabricated.
- The color and PL intensities of these hybrid films can be precisely controlled.
- The prepared PLFs were uniform and smooth with high visible light transmittance.
- They can be potentially used in the lighting and display fields.

ARTICLE INFO

Article history:
Received 5 March 2017
Received in revised form 28 April 2017
Accepted 29 April 2017
Available online 2 May 2017

Keywords:
Quantum dots
Layer-by-layer assembly
Surface modification
Multicolor
Photoluminescent films

ABSTRACT

In this report, all-quantum-dot multilayer photoluminescent films (PLFs) based on two types of modified quantum dots (MA-C8-QDs and PEI-QDs) were fabricated through the layer-by-layer (LBL) self-assembly method, providing a new kind of luminescent material with emission color covering blue to red spectral region. Aqueous QDs with high stability and photoluminescence properties were obtained by an efficient phase transfer, followed by fabrication of $(PEI\text{-}QDs/MA\text{-}C8\text{-}QDs)_n$ PLFs with alternate adsorbing the layer of the MA-C8-QDs endowed with negative ($—COO^-$) charges and PEI-QDs endowed with positive ($—NH_3^+$) charges using electrostatic interactions between each layer. The resulting single color films preserved good color purity and strong luminescence of original QDs, PL intensities increased linearly with the number of bilayers n, which indicated that growth of the film is regular and uniform. In addition, the uniform and smooth PLFs as prepared have high visible light transmittance. Furthermore, by emission tuning, multicolor and white light-emitting PLFs with the color coordinates at (0.3292, 0.3418) have been easily obtained by assembly of two types of modified red, green, blue QDs. Therefore, these PLFs (especially white-light PLFs) show promise for the development of novel multiplexed biological sensors, full-color displays, intelligent response, photonic, and optoelectronic devices.

1. Introduction

Novel materials based on colloidal semiconductor nanocrystal quantum dots (QDs) are attracting considerable interest of applications in the optoelectronic, including light-emitting diodes (LEDs) [1–8], solar cells [9], optical modulators [10], photoconductors [11], and lasers [12]. For the inherent merits of QDs, QD films have the advantageous features in the field of luminescent materials. Much effort was undertaken to prepare well-defined ultrathin QD films that may be used to explore potential applications in solid-state lighting and displays [13–16]. In order to realize full-color displays and lighting applications with QDs films, a method for the deposition of homogeneous and uniform QD layers with well-defined internal structures over a large area with patterning capability should be developed. As a facile, viable, and versatile technology for the preparation of many different multi-layers with nanosized objects such as nanocrystallites, polymers, nanoparticles, nanosheets, other functional components on various substrates in desired configurations, the layer-by-layer (LBL) self-assembly method is considered to be one of the most promising and feasible techniques [17–24]. Based on specific interaction forces between each deposited layer such as electrostatic

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http://dx.doi.org/10.1016/j.cej.2017.04.137
1385-8947/

interactions [25], covalent bonding [26], or hydrogen bonding [27], each QDs layer attracts only the layer with opposite charges by LBL self-assembly method. It can finely control the tuneable design of different QDs with desired structures and properties [23,28,29], and maintain QDs's excellent luminescence properties from each layers. Therefore, this method can be used to get nano-films with uniform internal structure with controllable structure and color over a large scale [30].

Some researchers have fabricated hybrid films composed of QDs and polymers recently based on LBL method [31–34]. For example, monoalkyl maleate amphiphilic surfactants were used to obtain water soluble QDs with high fluorescence intensity, good stability and surface functionalization, moreover, an inspiring luminescent planar plate was obtained by LBL assembly of multilayer photoluminescent films [35]. The optical and thermal stability of QDs are not changed during the assembly process, suggesting that this kind of hybrid quantum dot light emitting film has the properties of UV resistance and thermal resistance. However, for these hybrid films, several challenges remain to be resolved, for instance, this method usually requires a polymer layer with opposite charges, which may affect the optical properties of the entire film. And the miscibility, aggregation problems of QDs with polymers, intertwist of flexible polymer chains, can lead to difficulties in controlling homogeneous architecture and fluorescence concentration quenching of QDs in the polymer matrix. In regard with these problems, there have been some attempts to create QDs-based hybrid films combining QDs with inorganic matrices to avoid the above problems by the LBL self-assembly method [36–40]. However, if all QD multilayer films can be assembled, the above-mentioned process is complex, cumbersome, and pointless. Therefore, how to fabricate a QDs-based luminescent film with desirable compatibility, stability, and processing properties remains a challenge and it is particularly necessary to make all the quantum dots in order to improve the application potential of quantum dots in optoelectronic devices.

Aiming at a simple preparation of such films, we fabricate multilayer photoluminescent films (PLFs) which just rely on modified quantum dots rather than organic polymer or inorganic layers. All QD multilayer PLFs were fabricated by LBL assembly method using electrostatic interactions between each layer through the sequential deposition of oppositely charged QDs onto the substrates. Using the monoalkyl maleate (MA-C8) to surface modify pristine QDs (capped with oleic acid), we obtain the MA-C8-QDs capped with negative (—COO^-) charges dispersing in water (pH 8). The hydrophobic layer of the QDs was exchanged with amphiphilic hyperbranched polyethyleneimine (PEI) to get PEI-QDs endowed with positive (—NH_3^+) charges dispersing in water (pH 5) [41] (Fig. 1). QDs were fabricated into functional (PEI-QDs/MA-C8-QDs)n PLFs by alternate adsorbing the layer of the MA-C8-QDs and PEI-QDs through electrostatic interactions between each layer. By doing so, mono-color PLFs were fabricated by assembly of same color PEI-QDs and MA-C8-QDs. Multicolour and white-light PLFs were further obtained by assembly of variously color PEI-QDs and MA-C8-QDs (red, green and blue emission). Therefore, the work presented here provides a simple and convenient approach for the design and fabrication of all QD PLFs with high performance, which can be served as promising materials for the integration of multicolor optical and display devices.

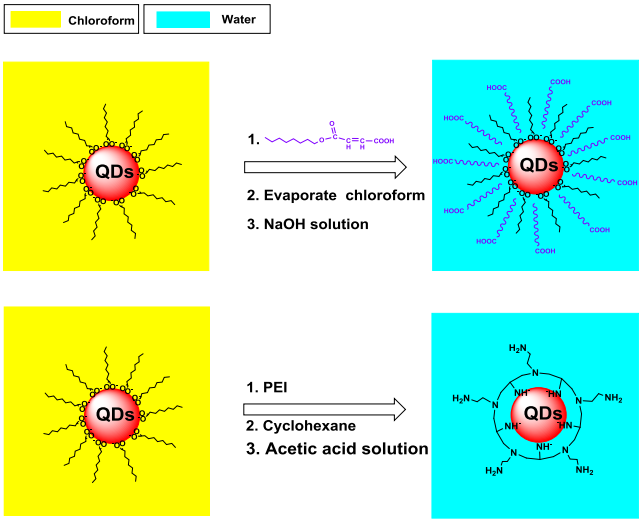

Fig. 1. Key steps in the formation of MA-C8-QDs (upper) and PEI-QDs (bottom).

2. Experimental

2.1. Materials

The raw materials used in the experiment were as follows: cadmium oxide (CdO, 99.99%), zinc oxide (ZnO, 99.9%, powder), sulfur (S, 99.98%, powder), 1-octadecene (ODE, 90%), paraffin oil (99.5%), oleic acid (OA, 90%), and selenium (Se, 99.99%, powder) were purchased from Aldrich. Maleic anhydride (MA, analytical reagent (AR)), polyethyleneimine (PEI, AR), *n*-octanol (AR), hexanes (AR), acetone (AR), acetic acid (AR), methanol (AR), chloroform (AR), sodium hydroxide (AR), ammonia water (28%), and concentrated sulfuric acid (98%) were purchased from Beijing Chemical Reagent Ltd., China.

2.2. Synthesis of hydrophobic QDs

Red CdSe/ZnS QDs (PL $\lambda_{max.}$ = 607 nm) and green CdSe/ZnS QDs (PL $\lambda_{max.}$ = 525 nm) were prepared by reported method in the previous literature [42]. Blue $Cd_{1-x}Zn_xSe$ QDs (PL $\lambda_{max.}$ = 455 nm) were synthesized according to the previous literature [43,44].

2.3. Surface modification of hydrophobic QDs

Monooctyl maleate (MA) was used as surface modifier to make hydrophobic QDs water-soluble in a phase transfer procedure. The synthesize of MA was carried out according to the previous report [45]. Briefly, mixed maleic anhydride (49.03 g, 0.50 mol) with N-octanol (65.12 g, 0.50 mol), after the mixture was heated at 80 °C for 1 h, the heptane (120 ml) was added into the reaction system, under stirring at 80 °C for 15 min. Finally, kept the solution static for 2 h at 15 °C, the crystals obtained were recrystallized in the same way, and the high purity of MA was obtained. Using the monoalkyl maleate and a typical procedure, finally aqueous MA-C8-QDs with the ability of being dispersed in water (pH 8) at different concentration (0.5, 1, 2 mg/ml) were obtained. By the similar method, using amphiphilic hyperbranched poly ethyleneimine (PEI) for phase-transfer of QDs into water (pH 5) through a simple, rapid method, we prepared aqueous PEI-QDs dispersed in water at different concentration (0.5, 1, 2 mg/ml) respectively [41]. The transfer is simple and quantitative, yielding a colorless phase and no aggregated particles, proving the success of the experiment.

2.4. LBL assembly of (PEI-QDs/MA-C8-QDs)n PLFs

For the layer-by-layer assembly of QDs on flat surfaces of glass slides, the substrates were cleaned with H_2SO_4 for 30 min followed by washing thoroughly with deionic water, immediately, after treatment with concentrated NH_3/30% H_2O_2 (7:3) for 30 min, the substrate surface was negatively charged. (PEI-QDs/MA-C8-QDs)n PLFs were fabricated according to the following cyclic procedure: