Quantum Dots-Based Flexible Films and Their Application as the Phosphor in White Light-Emitting Diodes

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ABSTRACT: Flexible luminescent materials, with the advantages of foldability and crack resistance, have attracted extensive interest owing to their broad application in collapsible optoelectronic devices. In this work, highly luminescent and flexible films were fabricated via self-assembly of triple building blocks: layered double hydroxide (LDH) nanoplatelets, polyvinyl alcohol (PVA), and quantum dots (QDs: CdTe or CdSe/ZnS), which show 2D ordered structure and finely tunable fluorescence (green, yellow, orange, and red). The resulting films display rather strong fluorescence and high fluorescence quantum yield (PLQY), which can be attributed to the uniform dispersion of QDs within the inorganic–organic hybrid matrix. Furthermore, we incorporated the red-emitting LDH/(PVA-CdSe/ZnS) film with the commercialized white light-emitting diodes (WLED) and obtained significantly improved color-rendering property through modifying its spectral distribution. In addition, the LDH/PVA-QDs films display high photo- and thermostability. Therefore, this work provides a facile approach for the design and fabrication of clay–polymer–QDs hybrid luminescent films with exceptional light emission, flexibility, and stability, which can serve as promising materials for the integration of WLED illumination devices.

1. INTRODUCTION

Semiconductor quantum dots (QDs) have received much attention over past decades because of their unique size-dependent optical properties. Compared with traditional organic fluorophores, they offer several advantages including flexible photoexcitation and sharp photoemission as well as superb resistance against photobleaching. Due to the inherent merits of QDs, they are promising candidates in optoelectronic devices, nonlinear optical devices, and biological labels. Generally, highly fluorescent QDs can be prepared by using colloidal chemistry approaches (e.g., organometallic routes and aqueous synthesis), but how to stabilize these QDs into a matrix is a crucial issue for their practical applications in solid-state devices. Compared with traditional devices, flexible luminescent materials possess the advantages of foldability and crack resistance and can be potentially used in collapsible optoelectronic devices. Although several approaches involving QDs and organic polymers have been developed for the assembly of flexible film materials, they usually suffer from phase separation, aggregation of QDs, and/or decreased fluorescence quantum yield (PLQY). Using a casting process, Tetsuka et al. reported an alternative method to stabilize QDs in organic polymers by the incorporation of some inorganic clays. Such an inorganic–organic route enhances physical stability and compatibility, but the nonuniformity and aggregation are still inevitable for the resulting film materials. Therefore, how to fabricate QDs-based luminescent films with desirable architecture, high flexibility, and stability remains a challenging goal.

Colloidal “bottom-up” synthesis and the self-assembly technique offer a facile approach for the ordered fabrication of functional building blocks on a small length scale, which make a significant impact on the development of new materials and devices. The combination of QDs within a sophisticated 2D matrix composed of polymer/inorganic material by virtue of the self-assembly technique provides a suitable approach for achieving well-stabilized and flexible luminescent films. Among inorganic counterparts, layered double hydroxides (LDHs) as 2D building blocks would be favorable to obtain hybrid films with high degree of ordered sequence. Recently, our group has explored flexible and self-standing films by assembly of LDH nanoplatelets and acetate polymers with superb mechanical property and oxygen resistance behavior. This further motivates us to take the challenge of fabricating LDH nanoplatelets/polymer-QDs composite films by alternate assembly of positively charged LDH nanoplatelets and negatively charged polymer–QDs clusters, which would exhibit the following advantages: (1) the 2D architecture of LDH/polymer–QDs film facilitates a double-confined microenvironment for the highly ordered distribution of interlamellar QDs,
which would give rise to high PLQY; (2) the light emission can be precisely controlled by changing the type/content of QDs with potential employment in white light-emitting diodes (WLED); (3) the hybrid films may own high photostability, thermostability, and mechanical property, as a result of the unique rigid LDH/flexible polymer architecture.

In this work, we report the highly luminescent and flexible films based on LDH nanoplatelets and polyvinyl alcohol (PVA)–QDs (CdTe or CdSe/ZnS) clusters, which show 2D ordered structure and finely tunable fluorescence. The hybrid films with green, yellow, orange, and red color luminescence were fabricated by using QDs with different particle sizes. A strong light emission and large PLQY were obtained for these films, close to those of QDs solution samples, indicating these QDs are highly dispersed in such an inorganic–organic hybrid matrix. Furthermore, we incorporated the red-emitting LDH/(PVA-CdSe/ZnS) film with the commercialized WLED and obtained largely improved white light via compensating its red-light range. In addition, the LDH/PVA-QDs films display dramatically enhanced photostability and thermostability, in comparison with the binary composition films (LDH/QDs film or PVA/QDs film), which would guarantee their practical application.

2. EXPERIMENTAL SECTION

2.1. Materials. Alk(Te)3, Cd(ClO4)2·6H2O, CdO, Se, mercapto-
succinic acid, oleic acid (OA), 1-octadecene (ODE), and polymaleic acid n-hexadecanol ester (PMAh) were purchased from Sigma Aldrich. The following analytical grade chemicals were used without further purification: Mg(NO3)2·6H2O, Al(NO3)3·9H2O, NaOH, ZnO, sulfur, and hexanes. Deionized water was used in all the experimental processes. All organic chemical compounds were purified using standard procedures prior to use.

2.2. Synthesis of the LDHs Nanoplatelets and QDs. Synthesis of MgAl(NO3)2-LDH Nanoplatelets. The synthesis of MgAl-LDH was similar to that described in our previous work.14 Typically, an aqueous solution (40 mL) containing Mg(NO3)2·6H2O (0.002 mol), Al(NO3)3·9H2O (0.001 mol), and a NaOH solution (0.06 mol; 40 mL) were added into a colloidal mill simultaneously. The rotating speed was 3000 r/min and was kept for 2 min. The mixture was sealed in a Teflon-lined stainless steel autoclave and heated at 100 °C for 24 h. The resulting MgAl-LDH was washed with water and dried in air at 60 °C.

Preparation of CdTe QDs. The aqueous synthesis of mercapto-
succinic acid modified CdTe QDs was referenced to the reported method.15 In a typical synthesis, 0.985 g (2.35 mmol) of Cd(ClO4)2·6H2O was dissolved in water (125 mL); 0.278 g of mercaptosuccinic acid stabilizer was added under stirring, followed by adjusting the pH value to be 11 with addition of a NaOH solution (1.0 M). The solution was placed in a three-necked flask fitted with septum valves and was deaerated by N2 bubbling for 30 min. Under stirring, CdTe gas generated by Al2(Te)3 and H2SO4 was purged into the solution by H2 for 2 min at 25 °C. The resulting CdTe QDs precursor was formed at this stage. The formation and growth of CdTe QDs proceed on reducing at 100 °C under open-air conditions with an attached condenser. The fluorescent color of CdTe QDs solution gradually changes from green to red upon increasing reducing time.

Preparation of CdSe/ZnS QDs. The synthesis of CdSe solution was the same as the previous report.6a By choosing CdSe as the core, CdSe/ZnS core–shell QDs was synthesized. A typical synthesis was performed as follows: 3 mL of ODE and 1.0 g of OA were loaded into a 25 mL reaction vessel. The CdSe QDs in hexanes (2.7 × 10−3 mol) were added, and the system was maintained at 100 °C under N2 flow for 30 min to remove hexanes and other undesired materials. The solution was heated to 160 °C under N2 flow for the growth of ZnS shell. At 180, 200, 220, 240, and 250 °C, the Zn and S precursors (Zn precursor was prepared by dissolving ZnO in the mixture of OA and ODE at 310 °C while S precursor by dissolving sulfur in ODE at 150 °C) with the volume of 0.52, 0.77, 1.10, 1.45, and 2.00 mL was added, respectively. Subsequently, hydrophilic QDs were obtained by using amphiphilic oligomer (PMAh) similar to the previous report with some modification.16a,b Typically, 0.5 mL of QDs (0.01 mmol, dispersed in chloroform) was added into PMAh solution in chloroform (0.08 mmol, 5 mL) and stirred at room temperature for 24 h in a closed container. The chloroform was then slowly evaporated by rotary evaporation, and the remaining QDs were dispersed in ammonia–water (pH = 9) with sonication to obtain a clear and colored QDs solution. To remove possible contaminants, the solution was passed through a 0.22 μm nylon syringe filter. Finally, the solution was centrifuged for 30 min at 20,000 rpm to remove excess oligomers (repeated four times).

2.3. Fabrication of LDH/PVA-QDs Films via Layer-by-Layer Assembly or Drop-Casting Method. The polyethylene terephthalate (PET) substrate was cleaned thoroughly with deionized water. The substrate was dipped into a colloidal suspension of MgAl-LDH nanoplatelets (10.0 g dm−3) for 10 min followed by washing thoroughly and then was treated with PVA-QDs mixed solution (PVA: 20 g dm−3; QDs: 5 g dm−3) for another 10 min. Multilayer films of (LDH/(PVA-QDs)), were fabricated by repeating the above deposition process for n cycles. The resulting films were dried with a nitrogen gas flow for 2 min at 25 °C.

The drop-casting LDH/PVA-QDs films were prepared by dropping 5 mL of the mixture suspension (LDH: 10 g dm−3; PVA: 20 g dm−3; QDs: 5 g dm−3) onto a 28 cm2 substrate and dried at 60 °C for 12 h. The drop-casting PVA-QDs films were prepared by dropping 5 mL of the mixture suspension (PVA: 10 g dm−3; QDs: 2.5 g dm−3) onto a 28 cm2 substrate and dried at 60 °C for 12 h. The film thickness is ~10 μm, close to the layer-by-layer LDH/PVA-QDs sample.

2.4. Characterization. The solid UV–vis absorption spectra were collected in the range from 300 to 900 nm on a Shimadzu U-3000 spectrophotometer, with the slit width of 1.0 nm. The fluorescence spectra were performed on a RF-5301PC fluorospectrophotometer with the excitation wavelength of 360 nm. The fluorescence emission spectra are in the range from 400 to 750 nm, and the width of both the excitation and emission slit is 1 nm. The morphology of films was investigated by using a scanning electron microscope (SEM Hitachi S-3500) equipped with an EDX attachment (EDX Oxford Instrument Isis 300), and the accelerating voltage applied was 20 kV. The surface roughness data were obtained by using a NanoScope IIIa atomic force microscope (AFM) from Veeco Instruments. TEM images were recorded on a JEOL JEM-2100 transmission electron microscope with the accelerating voltage of 200 kV. The fluorescence image was observed using an OLYMPUS-BX51 fluorescence microscope. The photobleaching was tested by the UV lighting with CHF-XQ 500W. The Commission Internationale de l’Eclairage (CIE) chromaticity color coordinates, color rendering index (Ra), and color temperature (CCT) were record by Konica Minolta CS-2000.

3. RESULTS AND DISCUSSION

3.1. Fabrication of Single Color Luminescence LDH/PVA-QDs Films. Single color QDs (green, yellow, orange, and red) were first mixed with PVA solution to produce negatively charged polymer–QDs cluster suspension; subsequently, single color emission films were fabricated by LBL assembly of LDH nanoplatelets and respective PVA-QDs onto the PET substrate. Supporting Information Figure S1 displays the morphology of LDH nanoplatelets with uniform lateral particle size of 100 nm and above 90% transmittance in the visible-light region (400–800 nm). Supporting Information Figure S2 shows the TEM images of CdTe QDs with particle sizes of 2.7 nm, 3.2 nm, and 3.9 nm with (green), (yellow), and (orange) and CdSe/ZnS QDs with particle size of 9.4 nm, respectively, both of which give strong and narrow light emission under UV irradiation (365 nm; Supporting Information Figure S3). The fluorescence spectra of the PVA-QDs colloidal solution are rather close to those of
pristine QDs solution with the same concentration (Supporting Information Figure S4), indicating no quenching of QDs owing to the good inter solubility between PVA and QDs.

Taking the red film LDH/(PVA-CdSe/ZnS) as an example, Scheme 1 shows the multilayer assembly process via electrostatic LBL technique. The \((\text{LDH}/(\text{PVA-CdSe/ZnS}))_n\) \((n = 6-30)\) films deposited on PET substrate were monitored by UV–vis absorption spectroscopy, respectively (Figure 1A). The intensity of the absorption band at 589 nm correlates linearly with the bilayer number \(n\), indicative of a stepwise and regular deposition procedure with almost equal amount of CdSe/ZnS QDs incorporated in each cycle. The intensity of the luminescence peak at \(\sim 619\) nm for the \((\text{LDH}/(\text{PVA-CdSe/ZnS}))_n\) films also displays a monotonic increase along with \(n\) (Figure 1B). Figure 1C,D illustrate the photographs of the four single color films \((n = 30)\) under daylight and UV irradiation, respectively, which exhibit uniform morphology and homogeneous light emission with very strong brightness. The PLQY of these luminescence films \((\text{LDH}/\text{PVA-QDs})_{30}\) are calculated to be 26.4% (green), 35.9% (yellow), 27.7% (orange), and 21.8% (red), respectively, based on their UV–vis absorption and fluorescence spectra (Supporting Information Figure S5). This keeps at a high level compared with that of pristine QDs solution (green 34.9%; yellow 49.4%; orange 36.9%; red 30.8%; Supporting Information Table S1). To demonstrate the merit of this LBL deposition method, we also prepared the luminescence films by drop-casting method, in which the maldistribution and nonuniformity both in film thickness and light emission were observed Supporting Information Figure S6). The results indicate that the self-assembly of LDHs nanoplatelets with PVA-QDs cluster leads to a superior high dispersion of QDs in the inorganic–organic hybrid matrix.  

3.2. Structural Characterizations of LDH/(PVA-CdSe/ZnS) Films. The structural and morphological properties of LDH/(PVA-CdSe/ZnS) films were further studied. Figure 2A and Supporting Information Figure S7 show the typical top-view SEM images of the \((\text{LDH}/(\text{PVA-CdSe/ZnS}))_n\) \((n = 6-30)\) films with various bilayer number, displaying a homogeneous surface morphology. The films thicknesses with various \(n\) can be estimated from their side-view SEM images (Figure 2B; Supporting Information Figure S8). An approximately linear increase in thickness as a function of \(n\) was observed, with an average thickness increment of 0.34 \(\mu\)m per bilayer cycle (Supporting Information Table S2). The AFM topographical images (2 \(\mu\)m × 2 \(\mu\)m) of \((\text{LDH}/(\text{PVA-CdSe/ZnS}))_n\) films are illustrated in Figure 2C and Supporting Information Figure S9, from which the root-mean-square (rms) roughness increases gradually from 1.32 to 2.29 nm as the bilayer number varies from 6 to 30 (Supporting Information Table S1), indicating a relatively smooth surface of these films. Moreover, we can observe the monodisperse distribution of CdSe/ZnS QDs from AFM images (0.4 \(\mu\)m × 0.4 \(\mu\)m; Supporting Information Figure S10). The results above confirm the uniform and periodic layered structure of these films throughout the fabrication process. Furthermore, the \((\text{LDH}/(\text{PVA-CdSe/ZnS}))_{30}\) film...
shows a homogeneous red color with strong brightness under a fluorescence microscope (Figure 2D), indicating that the CdSe/ZnS QDs are distributed uniformly in this inorganic–organic hybrid matrix film.

### 3.3. Photo- and Thermostability of LDH/(PVA-CdSe/ZnS) Film

Photo- and thermostability are extremely important criteria in practical applications of photonic or optoelectronic devices. The fluorescence intensity of the (LDH/(PVA-CdSe/ZnS))30 film was recorded by UV light illumination as a photostability study. After a 2 h irradiation, its fluorescent intensity decreased only 2% (Figure 3A and Supporting Information Figure S11A), while 11.1% loss was found for the PVA-CdSe/ZnS film without LDH nanoplatelets. This verifies that the LDH/(PVA-CdSe/ZnS) system possesses a better UV-resistance stability than the PVA-CdSe/ZnS one. The reason for better photostability of the LDH/(PVA-CdSe/ZnS) film relative to the PVA-CdSe/ZnS one is likely attributed to the multiple protection effects of the polymer–LDH hybrid matrix upon QDs. For the PVA-CdSe/ZnS film, the configurational change of polymer under UV light irradiation would induce the aggregation of QDs; while in the LDH/(PVA-CdSe/ZnS) film, the LDH nanoplatelets further provide a rigid and confined 2D microenvironment for a uniform dispersion of QDs which suppresses their migration/aggregation under UV irradiation. The thermostability was also studied. It is interesting to see that the (LDH/(PVA-CdSe/ZnS))30 film undergoes an increase in luminescence intensity upon heating at 60 °C for 12 min (Figure 3B and Supporting Information Figure S11B) and maintains at 115% of its original value in the following time range (12–120 min). The increased luminescence in the LDH/(PVA-CdSe/ZnS) system is possibly related to the removal of adsorbed water molecules in the interlayer region which may cause the formation of localized electronic surface states and lower PL intensity. In contrast, for the PVA-CdSe/ZnS film, a significant decrease in its luminescence intensity was observed after a heat treatment at 60 °C, possibly resulting from the aggregation of CdSe/ZnS QDs in this disordered system. On the basis of the thermostability test (Figure 3B), the PVA-CdSe/ZnS film shows an 11% decrease in intensity after heating at 60 °C for 120 min, while the (LDH/(PVA-CdSe/ZnS))30 film maintains at 115% of its original value, although they have the same loading of QDs. It is proposed that the distribution of QDs within such an inorganic–organic hybrid matrix suppresses their mobility and therefore promotes the thermostability of the LDH/(PVA-CdSe/ZnS) film. We further heated the (LDH/(PVA-CdSe/ZnS))30 film from 23 to 80 °C and finally to 100 °C and found its PL intensity decreased gradually; however, a complete recovery to its original intensity was obtained after cooling to room temperature (Figure 3C). Moreover, after 20 such heating–cooling cycles, its luminescence intensity decreases only 5.74% (Supporting Information Figure S12). The storage stability test on the (LDH/(PVA-CdSe/ZnS))30 film shows that ~97.9% of its original fluorescence intensity remained after six months (Figure 3D). In addition, the measurements on mechanical properties (Supporting Information Figure S13) demonstrate that the tensile stresses (σ) required for plastic yielding of (LDH/(PVA-CdSe/ZnS))30 and PVA-CdSe/ZnS film are 50.5 and 17.6 MPa, respectively, and the elastic moduli (E) of the two films are 2.8 and 0.8 GPa, respectively. The results indicate that the LDH/(PVA-CdSe/ZnS) film owns both better tensile strength and ductility than the PVA-CdSe/ZnS film. The results above demonstrate that the LDH/(PVA-CdSe/ZnS) film possesses strong photostability, thermostability, and mechanical and storage stability. This can be attributed to the rigid and confined 2D microenvironment offered by LDH nanoplatelets in which an ordered and uniform dispersion of the PVA-CdSe/ZnS cluster is achieved with the absence of chromophore migration/aggregation upon external stimulation.

### 3.4. Incorporation of the LDH/(PVA-CdSe/ZnS) Film with the WLED

Recently, LEDs as solid-state light devices have attracted considerable interest because of their environmental friendliness, long lifetime, low power consumption, high efficiency, and fast response. The commercialized WLEDS are normally based on InGaN blue chips with yellow-emitting Ce3+-doped Y2O3:Ce (YAG:Ce) phosphors. Although this WLED system exhibits high luminous efficacy and good stability, its optical properties (e.g., color rendering index (Ra), color temperature (CCT), and chromaticity color coordinates (CIE)) are not satisfactory due to the deficiency in the green and red region, which will deteriorate the illumination quality and environmental friendliness. Moreover, a low value of Ra and/or large CCT of WLED also impose serious damage to human eyesight. Therefore, how to achieve WLED with satisfactory luminous quality is challenging.

To solve these problems, the blue/green/red phosphors including QDs have been applied to obtain a high value of Ra. For instance, A high efficiency WLED was developed with a large Ra value by using green- and yellow-emitting Sr5SiO4:Ce3+/Li+ and CdSe QDs. A WLED was fabricated with backlight units using green (CdSe/ZnS/CDSDs) and red QDs (CdSe/CdS/ZnS/CdZnS) based on blue LEDs. Ziegler et al. reported a blue LED by employing silica coated InP/ZnS QDs with a green (Sr2.94Al2O4:Eu0.06) and yellow phosphor (YAG:Ce). Although much progress has been made, color-rendering properties including Ra, CCT, and CIE are difficult to synchronously control. In this work, the red-emitting LDH/(PVA-CdSe/ZnS) film was employed to
incorporate with the commercialized WLED for the purpose of obtaining high luminous efficacy and improved color-rendering properties though compensating its red color region.

Figure 4A and Table 1 show that the CIE of the commercialized WLED is located at (0.2649, 0.2883), close to blue-white region due to the redundant blue ray and insufficient red light. When this WLED is coated by the (LDH/(PVA-CdSe/ZnS))18 and (LDH/(PVA-CdSe/ZnS))30 film, the CIE moves to (0.3477, 0.3302) and (0.3902, 0.3454), respectively, which is rather close to the white light region (0.3333, 0.3333). Moreover, the Ra index and CCT of the WLED is significantly improved from (74, 12052 K) to (91, 4789 K) (coated by the (LDH/(PVA-CdSe/ZnS))18 film) and to (92, 3442 K) (coated by the (LDH/(PVA-CdSe/ZnS))30 film), respectively (Table 1), indicating that the CCT moves to pure and warm white by virtue of the compensation of the red color region. Figure 4B shows the emission spectra of the commercialized WLED and its integrated device with the LDH/(PVA-CdSe/ZnS) film, which can be attributed to the uniform distribution of QDs within the inorganic–organic hybrid matrix. The LDH/(PVA-CdSe/ZnS) films exhibit excellent photo- and thermostability. The red-emitting LDH/(PVA-CdSe/ZnS) film was applied to incorporate with the commercialized WLED; the color-rendering properties including CIE, Ra, and CCT can be effectively improved though modifying its spectral distribution (compensation of red range). It is expected that these clay–polymer–QDs luminescent films can be potentially used in the WLED integrated devices.

4. CONCLUSION

In summary, we have fabricated flexible films by assembly of LDH nanoplatelets, PVA, and QDs on the PET substrate. The resulting films display rather strong fluorescence and high PLQY compared with the corresponding pristine QDs solution, which can be attributed to the uniform distribution of QDs within the inorganic–organic hybrid matrix. The LDH/(PVA-CdSe/ZnS) films exhibit excellent photo- and thermostability. The red-emitting LDH/(PVA-CdSe/ZnS) film was applied to incorporate with the commercialized WLED; the color-rendering properties including CIE, Ra, and CCT can be effectively improved though modifying its spectral distribution (compensation of red range). It is expected that these clay–polymer–QDs luminescent films can be potentially used in the WLED integrated devices.

ASSOCIATED CONTENT

Supporting Information
Partial characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the 973 Program (Grant No. 2014CB932104), the National Natural Science Foundation of China (NSFC), the Scientific Fund from Beijing Municipal Commission of Education (20111001002), and the Fundamental Research Funds for the Central Universities (ZD 1303). M.W. particularly appreciates the financial aid from the China National Funds for Distinguished Young Scientists of the NSFC.

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