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Research Article

Inkjet-Printed CdTe Quantum Dots-Polyurethane Acrylate Thin Films

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We demonstrated the inkjet-printed CdTe quantum dots-polyurethane acrylate thin films and their potential application in the display devices. The water soluble CdTe QDs were synthesized through the wet chemistry and the emission wavelengths can be freely tuned during the preparation process. Combining with the UV curable resin polyurethane acrylate, the QDs inks were prepared and the influence of diluent and water content on the performance of resultant films was studied. The tensile stress of the films cured from the QDs inks with diluent increased from 10.6 MPa to 27.5 MPa and the low water content led to uniform polymer matrix. Furthermore, the existence of diluent and low water content would all improve the fluorescence stability of the thin films. Finally, the thin films can be deposited on different substrates and well controlled to meet the RGB color standard, which will pave the way to a simple, low-cost, large-scale, and highly reliable method for the application of flexible displays.

1. Introduction

Quantum dots (QDs), in the size of 1–10 nm with 200 to 10000 atoms, are inorganic fluorescent nanomaterials composed of II-VI and III-V elements, such as CdSe, CdTe, ZnSe, InP, and InAs [1–3]. Therefore, QDs are also called "nanocrystals" and "artificial atoms." Recently, QDs have drawn extensive attention in various fields due to their unique optical-electrical properties [4–9]. For example, the size-dependant emission spectra of QDs can be freely tuned in the visible range during the synthesis process and excited by the certain wavelength [4]. Because of the high quantum efficiency and excellent color purity, QDs are recognized as one of the most promising photoelectric display materials [9–11].

The new types of QDs displays possess high color purity and saturation which can remarkably improve the color quality of current display technology, especially for the flexible devices [9–14]. QDs-polymer composite materials with unique mechanical, electrical, optical, and thermal properties have been widely studied around the world [13, 14]. These unique properties are related to a number of aspects such as the present status of QDs, the dispersion of QDs in the matrix, and the interaction between QDs and polymers [9, 10, 14]. Recently, UV curing resins are extensively used in the synthesis process of polymer nanocomposites which have the advantages of low-cost and energy efficient [15]. Compared with the traditional method of melt extrusion molding, the UV cured QDs luminescent materials have better QDs dispersibility and interface adhesion of polymer-nanoparticle [15, 16]. In order to achieve the maximum brightness in the display devices, many efforts have been made to improve the luminescent quality and quantum yields and reduce the loading rates [17–21].

In this paper, we systematically studied the preparation of inkjet-printed CdTe QDs-polyurethane acrylate thin films and the potential application as luminescent films in the display devices. The key factors that affect the mechanical, luminescent property and photostability of the resultant films were analyzed based on the different preparation conditions. The uniform and pure colors shown by different thin films under UV-light demonstrate the feasibility of application in the display devices. This study enables the development of

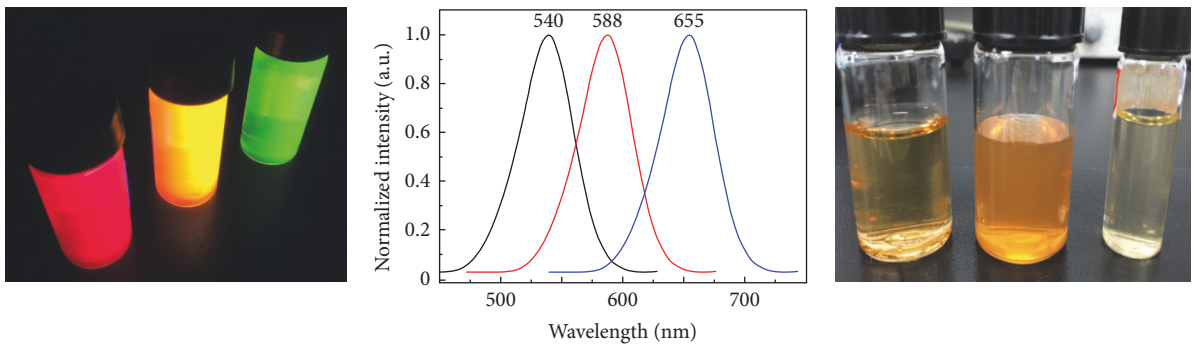


FIGURE 1: (a) Photograph and (b) the emission spectra of the as-synthesized water soluble CdTe QDs colloids under the UV-light (λ_{ex} = 365 nm). (c) Photograph of QDs inks under the room light.

novel and improved design of the UV curable oligomers/QDs in related light-emitting materials and devices.

2. Materials and Methods

2.1. Materials. Triton X-100, Tellurium powder (>96%), $CdCl_2 \cdot 2.5H_2O$ (>99%), $NaBH_4$ (96%), cyclohexane (99.9%), and 1-octanol (99%) were obtained from Sinopharm Chemical Reagent Co.; 3-mercaptopropionic acid (MPA, 99%), 6-aminocaproic acid (98.5%), and aqueous ammonia solution (30 wt.%) were supplied by Aladdin; polyurethane acrylate (named as WF-106, and the evocating agent is 1173) and Di (ethylene glycol) vinyl ether were purchased from Haiso Technology Co. Ltd., All other chemicals were used as received and the distilled water was used in entire experiment.

2.2. CdTe QDs Preparation. The water soluble CdTe QDs were synthesized according to the reference [16]. 23.0 mg of $CdCl_2 \cdot 2.5H_2O$ was dissolved in 50 mL of double distilled water in a round bottom flask, and then 45 μL of 3-mercaptopropionic acid (MPA) was added. The pH was adjusted close to 10 which was followed by N_2 bubbling for 30 min to remove the free O_2 in the solution. Then, 100 μL of the fresh-made NaHTe solution was mixed with the $CdCl_2$ solution in the flask within a condenser. The mixture was stirred at 100°C to reflux from 2 hours to 12 hours in order to harvest QDs with different emission wavelengths. Acetone was used several times to precipitate the raw QDs solution and the precipitate was separated by centrifugation. The resultant QDs were then dispersed into distilled water.

2.3. UV Curing QDs-Polyurethane Acrylate Thin Films Preparation. By combining the CdTe QDs with the UV curable resin polyurethane acrylate, several samples with different conditions were prepared to study the influence of emulsifier and water content on the property of composite films. 15 g of polyurethane acrylate was mixed with 5 mL of QDs, then 0.6 g of photoinitiator 1173 (3 wt.%) and 1 g of diluent Di (ethylene glycol) vinyl ether were added and further mixed. Vacuum distillation in the rotary evaporator was employed for the mixture to control the water content. All samples were exposed to the UV irradiation (λ = 360 nm) for 5 s during the UV curing process before further experiments. The thickness of the composite thin films was characterized as 60 μm. The films were coated according to [17].

2.4. Characterization. The photoluminescence spectra were obtained from luminescent spectrometer at room temperature using a UV-vis optic spectrometer (HR2000, Ocean Optics, USA); mechanical property tester (SANS CMT6503, China) was used to analyze the properties of the composite thin films, with 5 mm/min; Scanning Electron Microscope (SEM) (FEI Quanta 400 FEG) was utilized to characterize the morphology of thin films; the fluorescence spectra in photostability test were taken from the surface of the samples by using a UV-vis optic spectrometer (HR2000, Ocean Optics, USA).

3. Results and Discussion

We first prepared three CdTe QDs samples with different emission wavelengths by precisely controlling the synthesis process. The photograph of these samples under the UV-light (the excitation wavelength is 365 nm) are shown by Figure 1(a). These QDs colloidal solutions are highly fluorescent under the UV irradiation. From the emission spectra (Figure 1(b)), we can see that the emission wavelengths of CdTe QDs colloids corresponding to red, yellow, and green color are 655 nm (FWHM 35 nm), 588 nm (FWHM 33 nm), and 540 nm (FWHM 35 nm), respectively. After dispersing the water soluble CdTe QDs into the urethane acrylate prepolymer, stable colloidal solutions (QDs inks) were formed (Figure 1(c)). The result indicates that the prepolymer would not cause aggregation; hence the QDs inks would keep the highly fluorescent property. Further experiments also confirm that these "QDs inks" can be stored in dark bottles at room temperature for months without aggregations. This is because the polar structure of the prepolymer contributes to the dispersion and consequently stabilizes the QDs in the QDs inks.

UV curable resins such as polyurethane acrylate have been widely used in fiber coatings and electronic devices. Figure 2(a) shows the UV curing process and the resultant

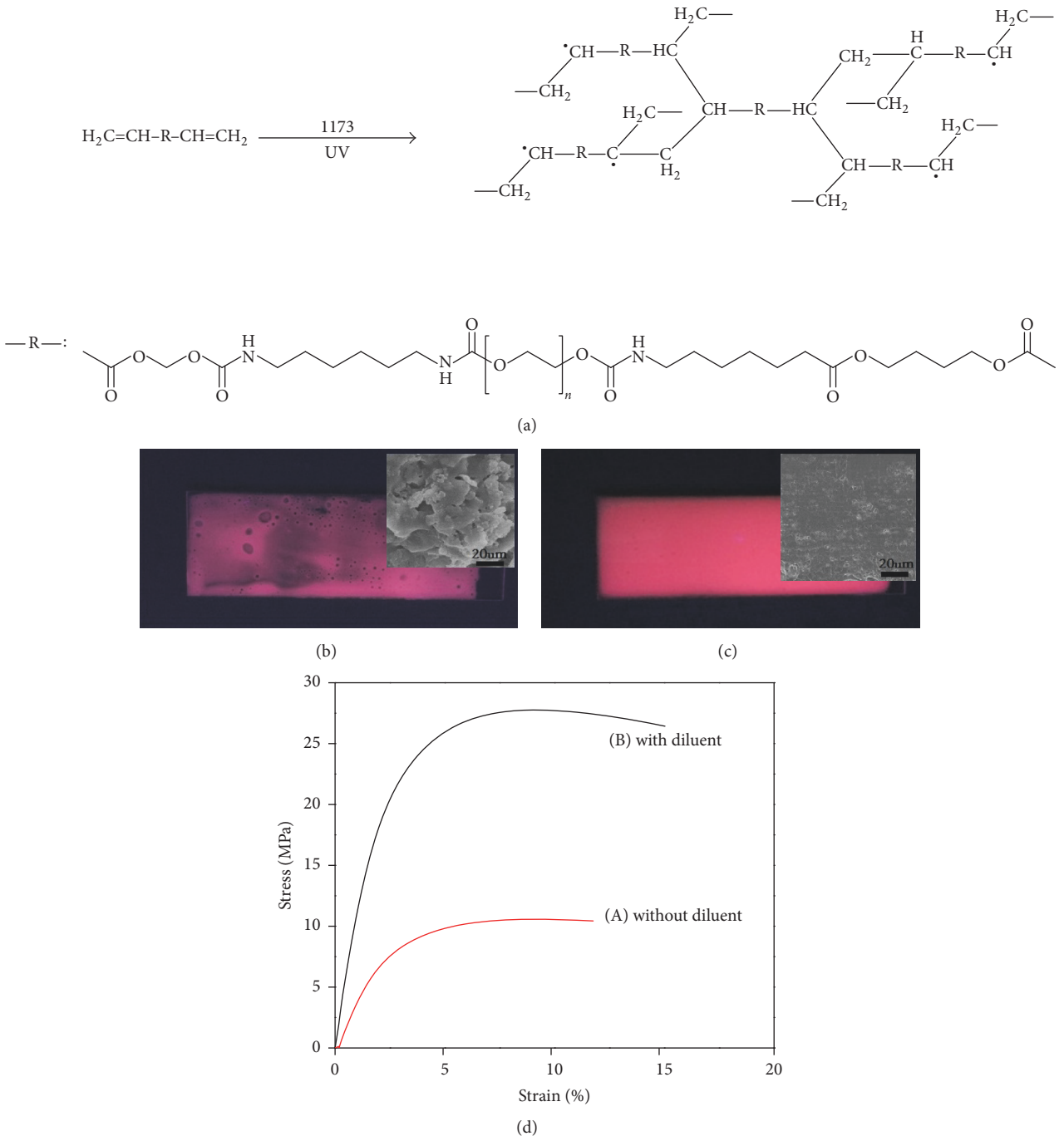
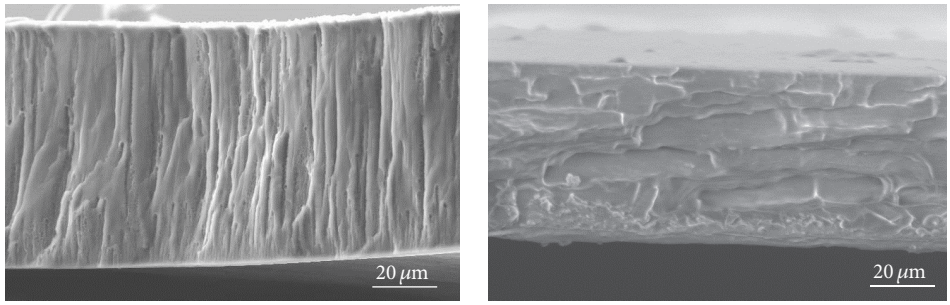


Figure 2: (a) The UV curing process and the resultant molecular structure. (b-c) Thin films cured from the QDs inks with (c) and without (b) diluent (inserts were SEM observations). (d) The influence of diluent on the mechanical strength.

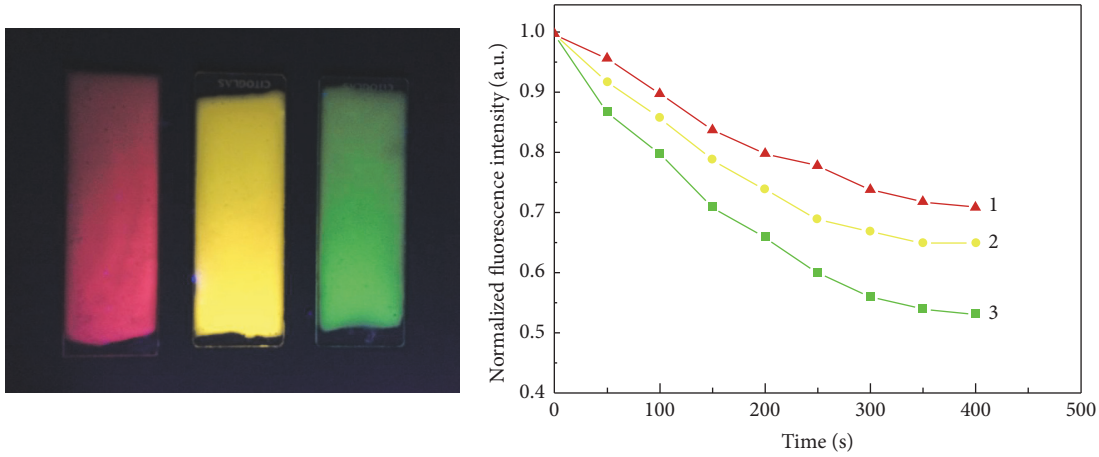
molecular structure when using the polyurethane acrylate 1173 as photoinitiator. This curable resin can be cross-linked to form an interconnected network structure, which thus possesses excellent mechanical property and flexibility. In addition, the polar molecular structure has good compatibility with the water soluble CdTe QDs, and therefore it can improve the dispersion of QDs in the QDs inks and adhesion between QDs and polymer.

During the UV curing process, diluent plays a significant role in the QDs inks. In this work, Di (ethylene glycol) vinyl ether was used to study the influence of diluent on the UV curing. Figure 2(b) shows a foamy morphology of the thin films on glass slide when the QDs inks were employed to prepare QDs-polyurethane acrylate thin films without diluent. By contrast, it was found that when 6% of the diluent is added to the QDs inks during the process,



(a) (b)

Figure 3: SEM cross-section of thin films cured from the QDs inks with high water content of 20% (a) and low water content of 5% (b).



(a) (b)

Figure 4: (a) Photograph of QDs-polyurethane acrylate luminescent films. (b) The photostability comparison of the UV curing polyurethane acrylate films. 1: QDs inks with diluent and 5% H_2O; 2: QDs inks with diluent and 20% H_2O; 3: QDs inks without diluent.

the resultant thin films show much better quality of free of porosity and uniform, as shown in Figure 2(c). These results demonstrate that the diluent has great impact on the quality and morphology of thin films, which is attributed to the change of viscosity after introducing diluent into the QDs inks.

Figure 2(d) shows the result of mechanical tests. We can see that the tensile stress of the thin films cured from the QDs inks without diluent only reaches 10.6 MPa, while the films with diluent reach 27.5 MPa. This result shows that the diluent Di (ethylene glycol) vinyl ether in the inks intensively affects the mechanical strength of resultant resin. QDs inks with diluent can form uniform polymer matrix during the UV curing process, while the QDs inks without diluent form polymer matrix with defects, resulting in the decreased mechanical strength.

During the UV curing process, water content in the inks also has important influence on the property of UV curable resin, as shown in Figure 3. The cross-section of thin films cured from the QDs inks with high water content of 20% shows defected polymer matrix structure (Figure 3(a)), while the cross-section of thin films cured from the QDs inks with low water content of 5% shows uniform polymer matrix (Figure 3(b)). It is hypothesized that the polymers can not form larger molecular weight with high amount of water content, so that the polymer matrix could not form uniform structure during the UV curable. In the experiment the water content of raw QDs inks is about 20% because QDs are first dispersed into water in the synthesis before the ink preparation. Due to the fact that high concentration of QDs inks results in better film quality, the QDs inks require further vacuum concentration before the UV curing process in order to produce thin films with great luminescent performance.

Finally, three CdTe QDs inks with different emission wavelengths were inkjet-printed on the surface of glass slides to produce the highly fluorescent thin films, as shown in Figure 4(a). One can see the films present uniform and pure red, yellow, and green colors. Figure 4(b) shows the results of the time-resolved photostability experiment about three QDs-polyurethane acrylate thin films with different preparation conditions. We can see that the fluorescence intensities of the films decrease under the continuous excitation due to the defects on the surface of QDs [11–14]. The difference between the decay curves of samples 2 and 3 indicates that diluent influences the dispersion status of QDs thereby improving the fluorescence stability. The difference between those of

samples 1 and 2 indicates that the lower water content can also improve the fluorescence stability. These improvements are extremely helpful for the fluorescent devices which are working under continuous excitation conditions. These inkjet-printed CdTe quantum dots-polyurethane acrylate thin films can be easily applied on different substrates (i.e., flexible substrate) and develop a simple, low-cost, large-scale, and highly reliable method for the application of flexible displays.

4. Conclusions

In conclusion, we proposed inkjet-printed CdTe QDs-polyurethane acrylate thin films. The water soluble CdTe QDs were obtained and the emission wavelengths can be freely tuned during the preparation process. Combining with the UV curable resin polyurethane acrylate, the QDs inks were prepared and the influence of diluent and water content on the performance of resultant films was studied. The results show that the existence of diluent and low water content can improve the quality and photostability of the thin films. Finally, the thin films can be deposited on different substrates and well controlled to meet the RGB color standard, which will pave the way to a simple, low-cost, large-scale, and highly reliable method for the application of flexible displays.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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