**ABSTRACT**

Mercaptoacetic acid-stabilized CdTe quantum dots (QDs) are prepared directly in aqueous solution. The multi-layer films of acrylate copolymer and CdTe nanoparticles were obtained by the layer-by-layer electrostatic self-assembly. It is shown that positively charged acrylate copolymer can be directly assembled outside the anionic CdTe QDs through an electrostatic force. The optical properties of the CdTe nanoparticles and the film build-up are monitored by employing the absorption and fluorescence spectroscopy. The deposition process is linearly related to the number of bi-layers as monitored by UV-vis absorption spectroscopy. The fluorescence intensity of ultrathin film rises with the DM content (9.69%, 16.29%, and 36.55%) in the acrylate copolymer and the photoluminescence spectra of multi-layers exhibit a red shift, indicating the enhancement of electrostatic forces between the carboxyl groups of thioglycolic acid capped on CdTe quantum dots and quaternization acrylate in cationic copolymer. The electrostatic interaction on the surface of the CdTe was enhanced with the DM content in the copolymer. Characterization of the multi-layer structures has been carried out by X-ray photoelectron spectroscopy. At the same time, the membrane morphology is investigated by atomic force microscopy. Electrostatic forces between anions in CdTe nanocrystals and cations in the copolymer strengthen the stability of the inorganic/organic compound because it played the role of surface passivation in CdTe QDs.

**INTRODUCTION**

Fluorescent semiconductor nanocrystals (NCs), also referred to as quantum dots (QDs) have attracted a broad range of attention in the past decades due to their quantum confinement effect and the distinctive electro-optic and physico-chemical properties [1]. Compared with conventional organic fluorescent dyes, quantum dots are known to have advantages such as broad absorption spectra in combination with symmetric luminescence bands, narrow emission spectra with full width at half-maximum, higher photostability, and tunable luminescence depending only on their size. Strong luminescent QDs show many potential applications especially in light-emitting diodes [2], photonic crystals [3], nonlinear optical devices [4], solar cell [5] and biological labeling [6]. Mercaptoacetic (thioglycolic) acid capped QDs have higher photolu-
minescence efficiency [7], and negative charge surface, thus, they are selected for the study of the layer-by-layer self-assembly with the aid of polymers.

Over the last decade, a variety of methods have been developed to construct hybrid ultrathin films. Among the assembly techniques, the layer-by-layer self assembly seems to be the most attractive method owing to its simplicity and universality [8].

Lesser et al. [9,10] were the first to report on the preparation of thin films from water soluble and highly luminescent CdTe nanoparticles with different polycations. Meanwhile, they studied electroluminescence of different colours from polycation/CdTe nanocrystal self-assembled films. Covalently attached self-assembly multilayer film based on CdTe nanoparticles was fabricated by Zhang et al. [11].

Recently, a large number of ultrathin films have been reported to be composed of II-IV semiconductor nanocrystal with polymers [12-14], e.g., ultra-thin film of CdS particles and nitro-diazo resin [15], multilayer structure prepared by layer-by-layer self-assembly using CdSe nanoparticles, and conjugated polymers [16,17]. Our laboratory made luminescence material by self-assembly using polymer with organic dyes and luminescent compounds [18-20], as well. So far, no report has been found concerning the self-assembly and composite of CdTe quantum dots with quaternized copolymers containing 2-(diethylamino)ethyl methacrylate and various alkyl methacrylates. The copolymer based on N,N-dimethyl-ethylamine methacrylate and various alkyl methacrylates. The copolymer based on N,N-dimethyl-ethylamine methacrylate (PDM) is a cheap polyelectrolyte that can be easily obtained [21]. It is also a polymer with very good membrane-forming properties, and can be used as the active-layer material of the composite membranes.

In this work, we report the fabrication of multilayer composite films of a water-soluble acrylate copolymer and CdTe nanoparticles. The growth of membrane assembly was monitored by UV-vis spectra and fluorescence spectrometry. In addition, elemental composition of the multilayer films was analyzed by XPS. At the same time, the membrane morphology was investigated by atomic force microscopy (AFM).

It is the originality and novelty of our work that CdTe has high quantum yield and tunable emissions in the visible range and the polymer has extensive applications, tunable physical properties, and good biocompatibility. On the basis of the versatile properties of polymer and the photoluminescence originating from the QDs, it is envisioned that these ultrathin films could be used in optoelectronic devices.

**EXPERIMENTAL**

**Materials**

Methyl methacrylate (MMA), 2-(dimethylamino)ethyl methacrylate (DM), 2-hydroxyethyl acrylate (HEA), n-butyl acrylate (BA), styrene (St), all of industrial grades were purchased from Beijing East Chemical Industry Factory, China, and distilled before use. The initiator 2,2'-azo-bis-isobutyronitrile (AIBN, CR) was obtained from Shanghai No.4 Reagent & HV Chemical Co. Ltd. Tellurium powder (99.999%) was purchased from Shanghai Chemical Reagents Company. Thioglycolic acid (TGA) (90%), CdCl₂·2.5H₂O (99%), sodium borohydride (NaBH₄) (97%) were obtained from Chengdu Kelong Chemical and Technology Reagents Ltd. Co., China.

**Characterization**

Ultraviolet-visible (UV-vis) adsorption spectra were measured using a TU-1901 UV-vis spectrophotometer. Fluorescence spectra were performed with a Hitachi F-4500 spectrofluorimeter. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos XSAM 800 spectrometer. Atomic force microscopy (AFM) was obtained with a Seiko SPA-400. All optical measurements were performed at room temperature under ambient conditions.

**Synthesis of TGA-capped CdTe Nanoparticles**

The CdTe QDs were prepared according to the reported procedure [22]. At first, sodium borohydride was used to react with tellurium in water to prepare sodium hydrogen telluride (NaHTe). Briefly, 80 mg of sodium borohydride was transferred to a small flask, and ultrapure water was added. After 127.5 mg of tellurium powder was added to the small flask, the reaction was maintained at 0°C in ice bath for about
8 h. The resulting NaHTe was used immediately in the next step for preparation of CdTe QDs. At the same time, 113.1 mg (0.5 mmol of CdCl$_2$.2.5H$_2$O was dissolved in 180 mL of ultrapure water in a three-necked flask, and 1.2 mmol of TGA was added while stirring. Then the pH of the solution was adjusted to 11.2 by dropwise addition of 1M NaOH. Under the protection of nitrogen atmosphere, the freshly prepared 0.2 mmoL of NaHTe solution was added to the three-necked flask, and the mixture turned faint yellow. The CdTe precursor was refluxed at different times at 100ºC to obtain CdTe QDs with different size nanoparticles. In this work, we used the QDs with maximum emission wavelength at 545 nm (green).

### Copolymer Syntheses
Isopropanol was added to a 250 mL three-necked flask equipped with a magnetic stir bar. When it began to circumfluence, the monomer of acrylate and initiator in certain concentration were transferred to the three-necked flask. After 6 h, the production spilled when temperature was lowered to 40~50ºC. The details of the process may be referred to literature [23]. Copolymers of different contents of 2-(dimethylamino) ethyl methacrylate (9.69%, 16.29% and 36.55%) were synthesized by using this process.

Table 1 shows the copolymer components. These products were red-brown, and sticky, demonstrated well film-forming property. The molecular structure of the copolymer is shown in Scheme I.

### Quaternization of the Copolymer (C-CPA)
A sample (4.0 g) of copolymer was introduced into a three-necked flask and dissolved in THF (25 mL) under stirring at room temperature. Next, an excess ethyl bromide was added into the three-necked flask. The reaction was left stirring for 24 h, by which the quaternized polymer had precipitated from solution. Then, the product of quaternized polymer was recovered by the complete removal of the solvent and the unreacted alkyl halide, followed by drying under vacuum until a constant weight was achieved.

### Multi-layer Fabrication of CdTe/C-CPA
The fabrication process of CdTe/C-CPA multi-layer film is described as follows. First, quartz slides were immersed in a fresh piranha solution (1:3 ratio of H$_2$O$_2$ (30%)/H$_2$SO$_4$ (98%) ) and heated until no bubbles were released, then thoroughly rinsed with distilled water and dried. These substrates were then dipped alternately in an aqueous solution of 0.5 mg/mL cationic C-CPA$_1$ and an aqueous dispersion of CdTe (0.001M) for 20 min each, with

![Scheme I. The molecular structure of copolymer.](image-url)
intermediate water rinsing and vacuum. One cycle results in a “bi-layer” consisting of a polymer and a CdTe monolayer. Multilayer films could be formed by repeating these two steps in a cyclic fashion while 7 bi-layer films were fabricated.

RESULTS AND DISCUSSION

FTIR Study of Copolymer
The FTIR spectrum of copolymer is presented in Figure 1. Copolymer IR (KBr) v: 3442 cm\(^{-1}\) (OH), 2958.47 cm\(^{-1}\) (CH\(_3\)), 1734.87 cm\(^{-1}\) (C=O), 1602.88 cm\(^{-1}\) (C=C), 1454.96 cm\(^{-1}\) (C-H), 1166.88 cm\(^{-1}\) (C-O), 762.15, and 702.69 cm\(^{-1}\) (δ Ph-H).

Characterization of the CdTe Quantum Dots (QDs)
Figure 2 presents the typical evolutions of both the UV-vis absorption and PL spectra of TGA-stabilized CdTe nanoparticles as a function of reflux time in the
aqueous solution. As shown in Figure 2a, all the first electronic transition and the maximum have shifted to higher wavelengths, with prolonging the reflux time, indicating that the size of the CdTe quantum dots is gradually increased and the distribution of the particle size is gradually widened. Thus, the quantum dots of different sizes can also be excited by the same monochromatic light source. In the meantime, as it is evident in Figure 2b, the photoluminescence emission peak position of QDs exhibits red shifts from 515 nm to 579 nm. The red shift of the absorption excitonic peak indicates the increase of particle sizes due to the quantum confinement, which is controlled by prolonging the duration of reflux time [11].

**Growth of Negatively Charged CdTe with Cationic Copolymer Multilayers**

The structures for both negatively charged TGA and positively charged copolymer (C-CPA) are shown in Scheme II.

The UV-vis spectra of the aqueous solution of C-CPA and TGA-stabilized CdTe suspension used are shown in Figure 3. The absorbance peak at 227 nm is assigned to $\pi \rightarrow \pi^*$ transition of the St group, which accounts for 15-18% in the C-CPA. The band at 500 nm is assigned to the first exciton band of CdTe nanoparticles.

A set of absorption spectra of CdTe/C-CPA of different bi-layer films is presented in Figure 4. A

![Scheme II. The structures for both negatively charged TGA and positively charged C-CPA.](image1)

![Figure 3. UV-vis absorption spectra of CdTe and C-CPA.](image2)

![Figure 4. UV-vis absorption of self-assembly films of CdTe/C-CPA [B3: 36.55% DM].](image3)
good linear relationship between the absorbance and number of bi-layer of the films was obtained for CdTe/C-CPA (inset of Figure 4), indicating a stepwise and uniform assembling process. The absorbance of the CdTe/C-CPA film at 227 nm illustrates that the C-CPA is incorporated successfully into the film. The driving force for the assembly comes from the electrostatic interaction between the polycation of C-CPA and the negative CdTe.

**FluorescenceChance of the Self-assembly Membrane**

Figure 5 illustrates the fluorescence spectra of multi-layer films of CdTe/C-CPA. The PL intensity increases gradually with the number of bi-layers, as shown in Figure 5a. When the bi-layer number of the film of CdTe/C-CPA goes up from 1 to 7, the fluorescence intensity rises. Similarly, Figures 5b and 5c show that the fluorescence intensity is increasing when the bi-layer number is 1–7. In addition, PL intensity of the same layer of CdTe/C-CPA is increasing with the changing DM content from 9.69% and 16.29% to 36.55%, which is an indication of the positive charge increases with elevation of DM content of the copolymer. In addition, fluorescence intensity of membrane increases with the enhancement of the electrostatic interaction.

The copolymers with three different DM contents were used for LBL production of multi-layers with CdTe. As shown in Table 1, the fluorescence peak of the same layer shows red shifts with the augment of the DM content of cationic copolymer due to the larger size of the particles. This may suggest that energy should be transferred from smaller to larger particles and emission takes place at longer wavelengths [24]. Fluorescence intensity is in proportion with the DM content due to more active electrostatic interaction between CdTe and cationic copolymer.

**Characterization of X-ray Photoelectron Spectroscopy**

It is well-known that X-ray photoelectron spectroscopy is a powerful analytical technique for surface studies. Figure 6 shows that CdTe and C-CPA are successfully incorporated into the film, due to the appearance of characteristic peaks of: Cd 3d_{5/2} at 404.4 eV.
(Figure 6a), Te 3d_{5/2} at 575.3 eV (Figure 6c) and that of S 2p at 162.2 eV (Figure 6b). These results prove the existence of TGA-capped CdTe nanocrystals. The characteristic C 1s peak at 284.8 eV (Figure d) can be attributed to the C element of C-CPA. The XPS results confirm the fact that the CdTe/C-CPA micropattern is successfully fabricated on the quartz via ESA process.

**Appearance of Self-assembly Membrane**

The surface morphology of CdTe/C-CPA multi-layer was studied by AFM. The multi-layer films were deposited on glasses which were cleaned through the procedures similar to those used for Quartz substrates. Figures 7a and 7b present the typical tapping mode AFM images of one and ten bi-layer films, respectively. The surface topography of the first bi-layer membrane of CdTe/C-CPA is given in Figure 7a. There are some obvious disfigurements existing on the surface of the film. However, the surface becomes smoother and shows no obvious caves on the 10 bi-layers film sample (Figure 7b). This is ascribed by the reason that ESA process can repair the disfigurements automatically.

**Figure 6.** XPS spectra of CdTe/C-CPA which show (a) the characteristic Cd 3d_{5/2} peak from CdTe nanocrystal 404.4 eV, (b) the characteristic S 2p peak 162 eV, (c) the characteristic Te 3d_{5/2} peak from CdTe nanocrystal at 575.3 eV, and (d) the C 1s peak from C-CPA (16.29% DM) at 284.8 eV.
CONCLUSION

We have described a convenient ESA process to form multi-layers of CdTe nanocrystal and quaternization acrylate copolymer based on electrostatic reactions. Electrostatic forces between the anionic nanocrystal and cationic copolymer strengthened the stability of the inorganic/organic compound because it played the role of passivation of the surface of the CdTe nanoparticles. The electrostatic interaction on the surface of the CdTe nanoparticles was enhanced with the DM content in the copolymer. The results of CdTe/C-CPA multi-layer film were thoroughly characterized by UV-vis spectra, PL spectra, XPS and AFM data. These results suggest that the thin-films may find a promising application in multi-color electroluminescence devices.

ACKNOWLEDGEMENT

This work was supported by National Nature Science Foundation of China (no.50573050). Analytical test was set up with the help of Dr YF Tian and Dr MZ Chen (The Analysis Test Center of Sichuan University) to whom the authors are very grateful.

SYMBOLS AND ABBREVIATIONS

ESA : Electrostatic self-assembly
LBL : Layer-by-layer
XPS : X-ray photoelectron spectroscopy
AFM : Atomic force microscopy
UV-vis : Ultraviolet-visible
PL : Photoluminescence
C-CPA : Quaternization copolymer
NCs : Nanocrystals
QDs : Quantum dots
MMA : Methyl methacrylate
DM : 2-(Dimethylamino) ethyl methacrylate
HEA : 2-Hydroxyethyl acrylate
ST : n-Butyl acrylate (BA), and styrene
AIBN : 2,2’-Azo-bis-isobutyronitrile
TGA : Thioglycolic acid
NaBH4 : Sodium borohydride
THF : Tetrahydrofuran
Fwhm : Full width at half maximum

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