

# CdTe quantum dots/Poly (diallyl dimethyl ammonium chloride) multilayer films: preparation and application for gaseous sensors

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**Abstract**— CdTe quantum dots (QDs)/Poly (diallyldimethylammonium chloride) (PDDA) multilayer films (QDMF) have been self-assembled by layer-by-layer (LBL) technique. CdTe quantum dots (QDs) were synthesized by using Te, NaBH<sub>4</sub>, and CdCl<sub>2</sub> as precursors and mercaptopropionic acid (MPA) as stabilizer. The as-prepared composites were characterized by transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR), UV-vis adsorption spectrum (UV-vis), and Fluorescence spectrum (FS), respectively. It was shown that the self-assembled QDMF in this study could be used as gaseous sensors for detecting organic gases, such as ammonia, acetone, methanol and formaldehyde. The quenching mechanism of CdTe QDs multilayer films by formaldehyde was studied in detail and The detection limit was 10-236ppm.

**Keywords**— CdTe quantum dots, gaseous sensor; PDDA, QDMF.

## I. INTRODUCTION

A trend in current sensor development is miniaturization to obtain inexpensive and compact gas sensors that are robust and safe, have low power consumption and enable multiplexing of sensor arrays and remote sensing [1, 2]. Gas sensors play a key role in a variety of fields, such as environmental pollution monitoring, industrial process monitoring, leak detection of explosive gases, and medical breath analysis. In order to increase sensitivity, devices with nanostructure for gas sensors has shown lots of advantages[3].

From previous literatures, we can find that there are many gas detecting methods so far. But, compared with those traditional gas detection techniques, which are often costly, low sensitivity and time-consuming, semiconductor sensors have drawn a great deal of attention in recent years for its unique optical advantages. Semiconductor luminescent nanocrystals, known as “quantum dots” (QDs), exhibit unique optical and electronic properties, including high luminescent quantum yields, tunable emission, high photostability and relatively long emission lifetime. All these advantages explain the reason of its presence [4]. Furthermore, it has been used for energy conversion and storage[5-8], fabrication of optoelectronic device[9], and particularly, sensor applications[10-12].

Recently, a number of QD-based sensors have been reported for ions, [13] biomacromolecules, [14-16] and small organic molecules. [17] And, CdTe QDs have been proved to be a promising material as elemental building blocks for the next generation of nanodevices [18, 19]. Self-assembled multilayers by layer-by-layer (LBL) method are stable, well-ordered, easy to prepare and low cost, and have been extensively applied for the constructions of chemo- and bio-sensors [20, 21]. Another important feature of LBL is recharging of the surface at every step of the adsorption self-assembly, which results in oppositely charged molecules to be adsorbed in the next step with molecular order during the films fabrication process. Therefore the stable LBL method can encapsulate the QDs efficiently into flexible nanofilms (thickness below 60 nm) [22]. It has been also successfully applied to the preparation of multilayer films of polyelectrolytes with other materials such as proteins, graphite oxides, gold colloids, dyes and nanoparticles [23]. Many groups have developed QDs-based sensing systems for the detection of Hg<sup>2+</sup> [24-26] and Cu<sup>2+</sup> [27-29] based on the fluorescence quenching of QDs.

In this paper, CdTe QDs multilayer films was fabricated by the standard LBL assembly technique. The CdTe nanoparticles with negative charged in the presence of MPA can serve as the anionic entity needed in the multilayer fabrication technique.

Besides, The effects of assembling methods, concentration of PDDA and layer number of films on fluorescence intensity of QDMF have been studied.

## II. MATERIALS AND METHODS

### 2.1 Materials

Cadmium chloride (A. R.), sodium borohydride ( $\text{NaBH}_4$ , A. R.), tellurium powder (H.R.), mercaptopropionic acid (MPA, >90%) and sodium hydride (A. R.) were purchased from Sinopharm Chemical Reagent Company, Tianjin Guangfu Fine Chemical Research Institute, Tianjin Delan Fine Chemical Factory, Shanghai Jifeng Biotechnology Company and Tianjin Kermel Chemical Reagent company respectively. Poly (diallyl dimethyl ammonium chloride) (PDDA, G. R.) was obtained from Sigma Chemical Co. All reagents were used as received without further purification.

### 2.2 Synthesis of CdTe QDs coped with MPA

The method for the preparation of NaHTe was described elsewhere[30,31] with a few modifications. 40 mg of sodium borohydride was put into a small flask, followed by adding 0.5mL of secondary distilled water. After 15 mg of tellurium powder was added in the flask, the reacting flask was rapidly sealed via a rubber plug with a small long syringe pinhead inserted into the flask to discharge pressure from the resulting hydrogen. After 4-5 hours, the black tellurium powder disappeared and a white sodium tetraborate precipitate appeared at the bottom of the flask. The resulting NaHTe aqueous solution with light pink was obtained.

The CdTe QDs were prepared using a simple refluxing route in aqueous solution with some improvement [32]. The synthesized NaHTe was added into  $\text{CdCl}_2$  (0.173 mmol/mL) solution at pH 9.1 in the presence of MPA (80  $\mu\text{L}$ ) in  $\text{N}_2$  atmosphere. The CdTe precursor solution was heated to 96°C at different refluxing times. The whole process was carried out in  $\text{N}_2$  atmosphere.

### 2.3 Preparation of CdTe quantum dots/ Poly (diallyl dimethyl ammonium chloride) Multilayer films (QDMF)

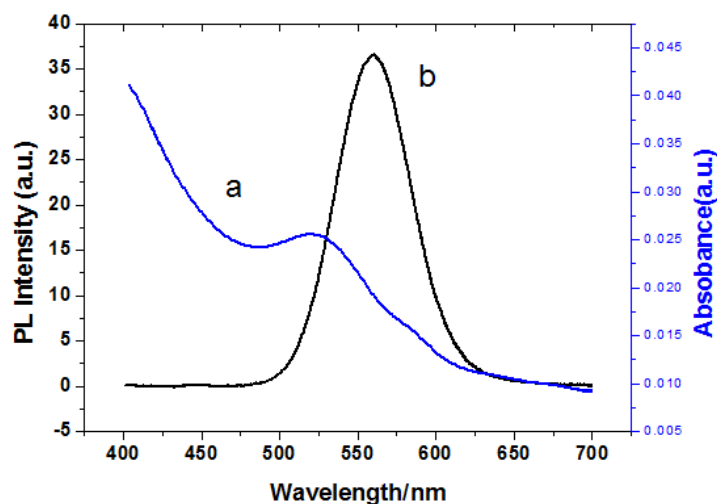
The glass substrates were pretreated according to the literature [33]with some modifications. The glass chips were ultrasonically washed with pure water and boiled for 30 min, after being immersed in  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$  solution with the volume ratio of 7:3. Finally, the chips were washed with DI water and dried with nitrogen. QDMF were prepared using a layer-by-layer procedure[34]. The chips were dipped in a PDDA aqueous solution for 20 min to modify a monolayer of positive PDDA. Then the modified substrates were rinsed with DI water several times to remove the physically absorbed PDDA, and dried under a stream of nitrogen. Then the chips were immersed in CdTe QDs aqueous solution to charge negatively QDMF were formed by repeating these steps in a cyclic fashion. The principle of multilayers' self-assembling was based on the electrostatic interaction between negatively charged QDs and positively charged PDDA.

### 2.4 Characterization

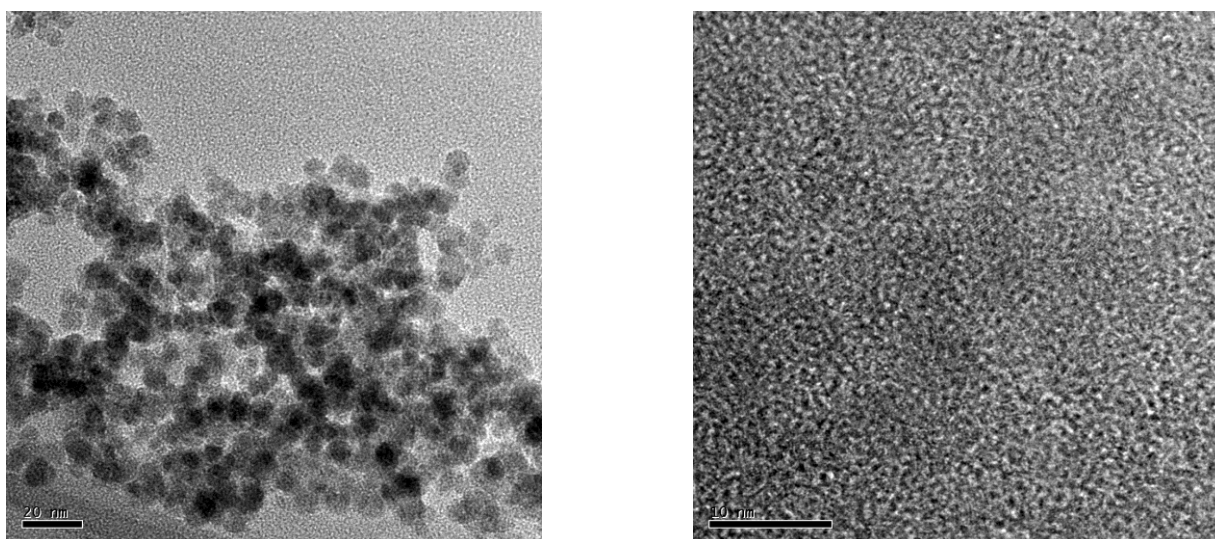
The transmission electron microscope (TEM) images were taken with a Hitachi-7650 electron microscope operated at an acceleration voltage of 100kV. Fourier transform infrared spectroscopy (FTIR) was performed using a FTIR-650 spectrometer. The UV-vis adsorption spectral values were measured on a Helios- $\gamma$  spectrophotometer. Fluorescence experiments were performed with the help of F-380 spectrofluorimeter.

### 2.5 Quenching

In this process, the prepared QDMF was taken in a bottle containing a certain amount of organic gases. After 40 minutes' standing, the change of fluorescence intensity of QDMF was detected by spectrofluorimeter to investigate the concentration of organic gases. Finally, the result of the detection reflects sensitivity of prepared samples.



**FIG. 1. UV-VIS ABSORPTION (a) and PL (b) SPECTRA OF AS-PREPARED CdTe AQUEOUS SOLUTION AT THE REFLUXING TIME OF 4H WITH EXCITATION WAVELENGTH OF 390 nm**



**FIG. 2. TEM IMAGES OF CdTe QDS (A), CdTe LATTICE STRUCTURE (B)**

### III. RESULTS AND DISCUSSION

#### 3.1 Optical feature of CdTe QDs and QCMF

Fig. 1 presents the typical absorption and PL spectra of CdTe QDs aqueous solution. It was found that the fluorescence intensity of CdTe quantum dot with 4 hours refluxing time was comparatively strong. The PL emission wavelength of QDs was 563 nm with a relatively narrow half peak width and best crystal quality, which is consistent with the literature report [35].

The distinct absorption (a) and PL (b) peaks of 0.024 a.u. and 38a.u. indicate that the QDs were highly monodispersed. The absorption shoulder of CdTe QDs was located at 525 nm, while the emission spectra display an emission maximum around 563 nm upon excitation at 390 nm. The size of CdTe QDs is estimated to be ca.3.4 nm in virtue of the following empirical formula according to previous report [31]:

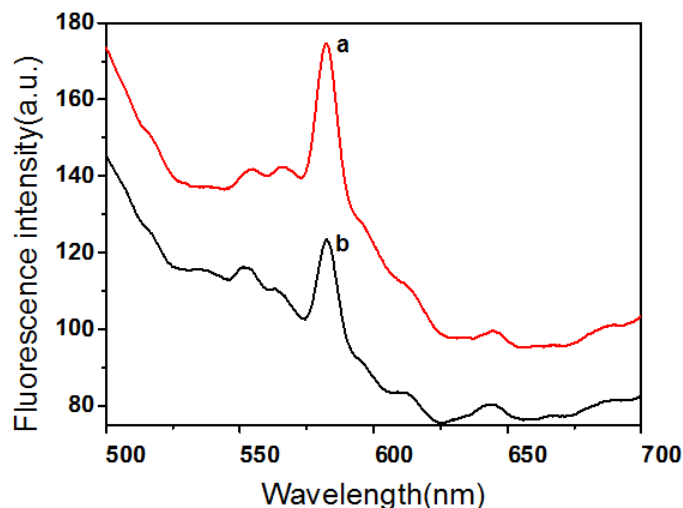
$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - 194.84 \quad (1)$$

Where D (nm) is the size of CdTe QDs, and  $\lambda$  (nm) is the wavelength of the first excited absorption peak of the corresponding sample. The TEM image of CdTe QDs is shown in Fig. 2. The QDs was deposited with a high monodispersion without particle agglomeration, which corresponds to the Fig. 1, and the size of QDs is in line with the estimated results from equation 1.

### 3.2 Effect of assembling conditions on FL intensity of QDMF

#### 3.2.1 Assembling styles

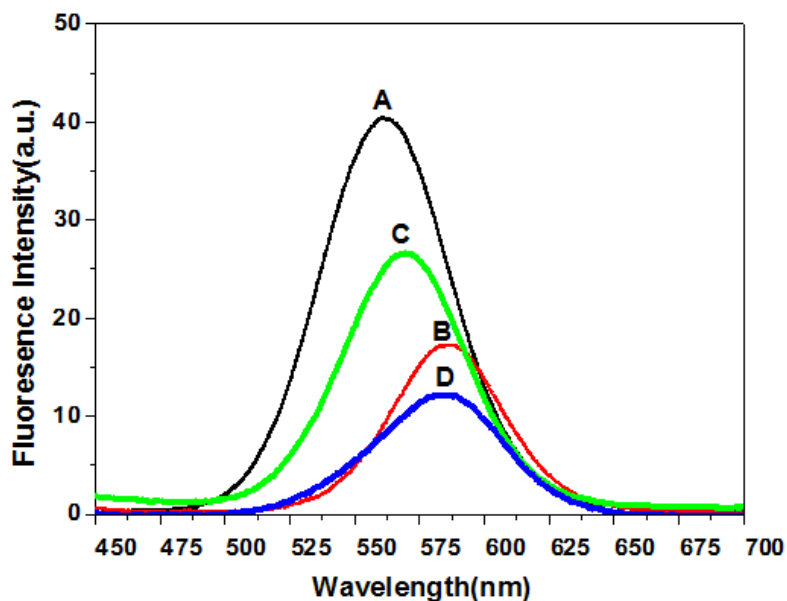
Two different assembling methods of QDs with PDDA were compared. First, aliquot of PDDA and CdTe QDs were dipped onto a glass chip by a pipette [32]. Second, the cleaned glass chip was immersed in positively charged PDDA and negatively charged QDs aqueous solution alternately [10]. It was found from Fig. 3 that the PL intensities of QDMF prepared by the two methods were 174 nm (a) and 123 nm (b), respectively, which indicates that the dip method was better than another one. In this study, the dip method was adopted for further experiment



**FIG. 3. FLUORESCENCE INTENSITIES OF QDMF BY DIFFERENT ASSEMBLING METHODS: (A) DIPPING QDS AND PDDA SOLUTION ONTO THE GLASS CHIPS AND (B) IMMERSING THE GLASS CHIPS INTO QDS AND PDDA SOLUTION. THE CHIPS WERE DEPOSITED 6 TIMES FOR EACH CONDITION.**

#### 3.2.2 The concentration of PDDA

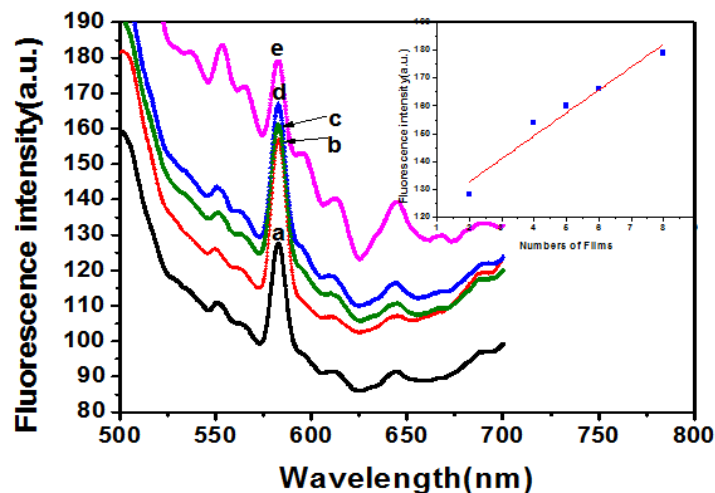
The influences of the concentration of PDDA on the PL intensity of QDMF are shown in Fig. 4. Note that the PL intensity of the QDMF increased remarkably with the increasing concentration of PDDA and reached a maximum at 0.03% (Fig. 4C), so it was chosen for the further experiment. In addition, all the CdTe QDs/ Polyelectrolyte multilayer film exhibited photoluminescent behaviors.



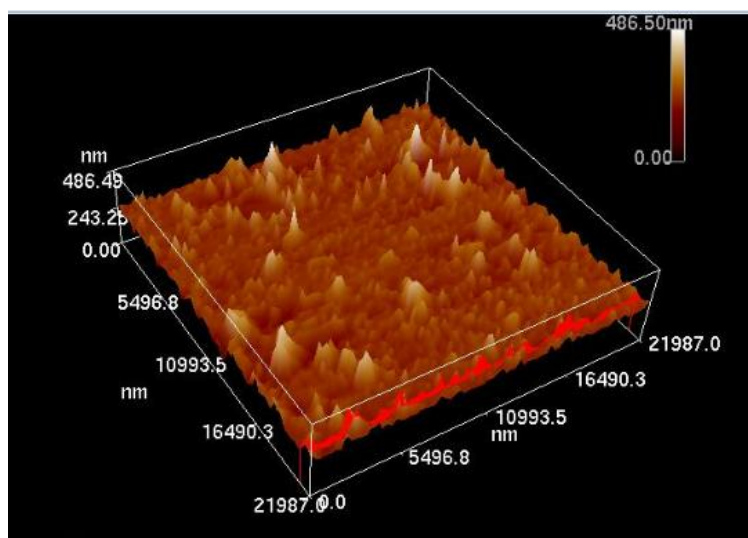
**FIG. 4. THE PL INTENSITY WITH DIFFERENT CONCENTRATION OF PDDA DEPOSING ON THE QDMF. (A) 0 PDDA, (B) 0.003% PDDA, (C) 0.03% PDDA, (D) 0.3% PDDA.**

### 3.2.3 Layer number of QDMF

The fluorescence intensity proportionately enhances along with the increasing of deposited QDs layer number as shown in Fig. 5. The PL intensity of QDMF can be adjusted by varying the number of deposited CdTe QDs layers. However, with the number of layers increased, the fluorescence emission peak at 550nm has a negative effect on the detection (detection accuracy). Therefore, in this study, six layers of QDMF is chosen for the further experiment.



**FIG. 5. FLUORESCENCE EMISSION SPECTRUM OF QDS-MULTILAYER FILMS WITH DIFFERENT QDS LAYERS. (A) 2-LAYER, (B) 4-LAYER, (C) 5-LAYER, (D) 6-LAYER, (E) 8-LAYER. INNER GRAPH IS THE RELATIONSHIP BETWEEN PL INTENSITY OF QDMF AND THE NUMBER OF QDS LAYERS. ( $n=5$ , RSD 5.47%).**



**FIG. 6. AFM PICTURES OF QDMF**

The AFM picture of CdTe QDs-multilayer films with 5 QDs layers are shown in Fig. 6. We can see that there are some peaks with different diameter on the surface of film, confirming that CdTe QDs were successfully grown in the reaction. The emergence of the larger peak on the surface of PDDA may be due to the aggregation of CdTe quantum dots in process of electrostatic self-assembly. However, Tanaka [33] pointed out the reason for this phenomenon. First, only one end of the Polyelectrolyte molecules was combined on the surface of the substrate, and second, many pendant groups combined with Polyelectrolyte molecules have coupled with substrate.

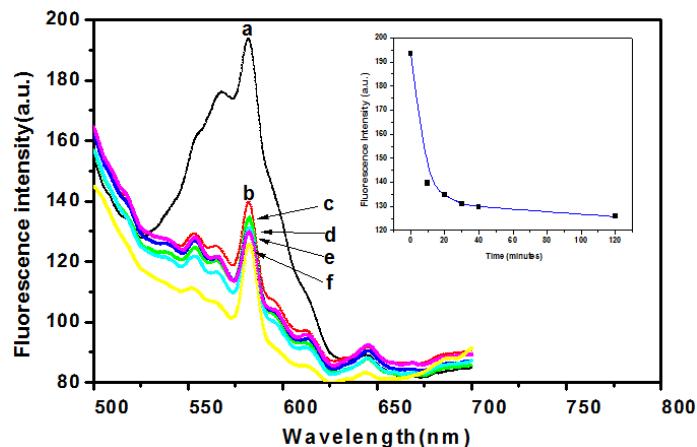
### 3.3 The quenching study of QDMF

#### 3.3.1 Different quenching time

Quenching time was an important factor for the interaction between CdTe QDs and ammonia. QDMF was reacted with ammonia gas for different time. The corresponding fluorescence spectra of multi-layers are shown in Fig. 7. The fluorescence intensity progressively decreases along with the increasing of the quenching time. As shown in the picture, the fluorescence

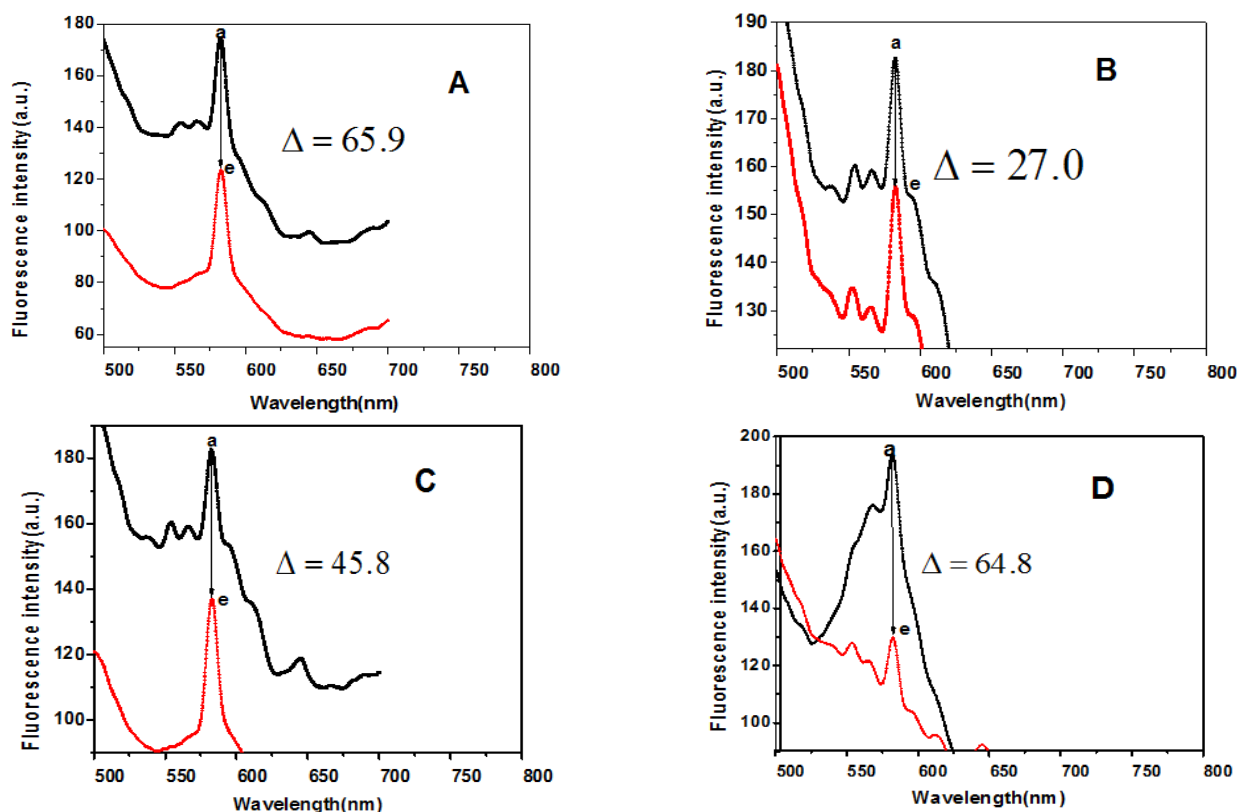
intensity dramatically decreases from ca.193.3 to ca.128.5 in the first 40 min, and there is no decrease of PL intensity when the quenching time exceeds 40 min. This indicates that the quenching of ammonia on the PL intensity of QDMF achieved saturation when the quenching time reached 40 min. Based on the above results, 40 min was adopted as the optimal quenching time.

### 3.3.2 Different organic gases



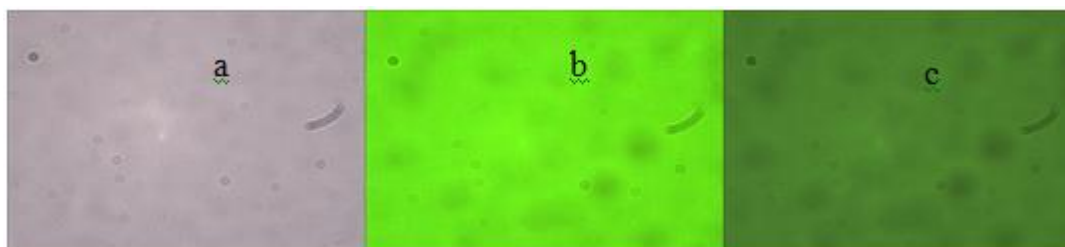
**FIG. 7. QUENCHED PL OF QDS-MULTILAYER FILMS BY AMMONIA GAS AT DIFFERENT REACTION TIMES. (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 40 min, (f) 2 h.**

Fig. 8 shows that QCMF was quenched by the four kinds of gases with different concentrations. All the gas molecules include the group of amidogen and carbonyl. PL intensity of QDMF (6 layer numbers for all the experiments) was decreased by all the quenching gases: (A) 65.9 a.u. by formaldehyde; (B) 27.0 a.u. by methanol; (C) 45.8 a.u. by acetone; and (D) 64.8 a.u. by ammonia. Therefore, the QDMF can be used as the sensors for certain gases with the group of amidogen and carbonyl, such as acetone, methanol, ammonia, formaldehyde, and so on.



**FIG. 8. QUENCHED PL SPECTRA OF QDMF BY DIFFERENT GASES AT QUENCHING TIME OF 40 MIN. (A) BY FORMALDEHYDE, (B) BY METHANOL, (C) BY ACETONE, (D) BY AMMONIA.**

### 3.3.3 The fluorescence image of QDMF

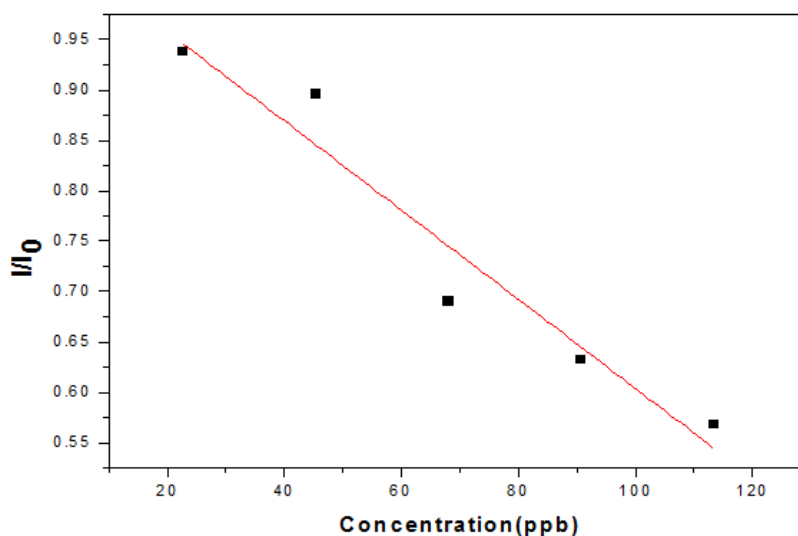


**FIG. 9. THE FLUORESCENCE IMAGE OF QDMF, BEFORE EXCITATION(a),UV(365nm) excitation(b), UV(365nm) EXCITATION AFTER QUENCHED BY METHANOL(c).**

In our previous work, a preliminary study on the detection effect of the current sensor has been implemented. In this process, commercial UV light is used to detect prepared samples under conventional conditions (without the aid of fluorescence spectrometer and other advanced instruments). Fig.9 shows that the prepared sensors have high detection ability for formaldehyde and other harmful gases. As a result, the family self-detection could be initially realized and the market has huge potentiality.

### 3.3.4 The detection limit of formaldehyde

To study the detection limit, the as-prepared QDMF and different amount of formaldehyde (10ul, 20ul, 30ul, 40ul, 50ul) were placed into a bottle for fluorescence quenching experiment. After 40 min reaction, the PL intensity of sensors was detected. Fig.10 shows the change curves of PL intensity of QDMF with different concentration of formaldehyde, and its kinetics can be expressed as:  $I/I_0 = 1.04586 - 0.00442 * CHCHO$  (ppb), where  $I$  and  $I_0$  are the PL intensity of QDMF (before quenching and after quenching, respectively). The detection limit was calculated to be 10-236ppm, which is far below the country safety standard (80ppm).



**FIG.10 THE FLUORESCENCE INTENSITY OF QDMF WITH DIFFERENT FORMALDEHYDE CONCENTRATION**

## IV. CONCLUSION

The layer-by-layer method was adopted to prepare the QDMF, which was built up with PDDA and CdTe QDs modified by MPA. Owing to electrostatic interactions between anionic QDs and cationic PDDA, the LBL method affords more stable coating than physical adoption. The standard LBL self-assembling technique has been proven to be a rapid and convenient way to produce complex layered and hybrid structures. The multicolor CdTe quantum dots were prepared using a refluxing method in aqueous solution with high PL intensity. The PL intensity of QDMF can be quenched effectively by the groups of amidogen and carbonyl. Organic gas molecules without carbonyl and amidogen groups have no effect upon the fluorescence quenching of QDMF. Thus, the self-assembled QDMF in this study could be used as gaseous sensors for detecting organic gases, such as ammonia, acetone, methanol and formaldehyde. And for formaldehyde, The detection limit was calculated to be 10-236ppm.

### ACKNOWLEDGEMENTS

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