石墨烯/CdTe 量子点复合物的合成及在克伦特罗检测方面的应用

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摘要： 成功地合成了石墨烯/CdTe 量子点复合物，并采用透射电镜、紫外吸收光谱、荧光发射光谱、荧光衰减曲线和 X 射线光电子能谱对产物进行了表征。透射电镜结果显示 CdTe 量子点被修饰于石墨烯的表面；X 射线光电子能谱结果表示石墨烯在合成过程中被还原，还表明在所合材料的表面具有羧基和羟基；荧光发射光谱和荧光衰减曲线的结果显示将 CdTe 量子点修饰于石墨烯表面显著提高了 CdTe 量子点的荧光性能。此外，基于克伦特罗和石墨烯/CdTe 量子点复合物之间形成的氢键，所合成材料可用于定量分析克伦特罗。克伦特罗对石墨烯/CdTe 量子点复合物具有显著的猝灭作用，荧光强度的降低(F_0/F)与克伦特罗之间存在良好的线性关系，线性范围为 7.22~108.30 $\mu mol \cdot L^{-1}$，检出限为 4 $\mu mol \cdot L^{-1}$。

关键词： 石墨烯/CdTe 量子点复合物；合成；表征；荧光探针
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Graphene/CdTe Quantum Dots Composites: Synthesis and Application on Clenbuterol Detection

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Abstract: Graphene/CdTe quantum dots composites had been successfully synthesized, which was characterized by using transmission electron microscope, absorbance spectrum, fluorescence emission spectrum, fluorescence decay curve and X-ray photoelectron spectroscopy. Transmission electron microscope results indicate that CdTe quantum dots have successfully decorated on the surface of graphene. X-ray photoelectron spectroscopy results indicate that graphene has been reduced and have carboxyl and hydroxyl groups on its surface. Fluorescence emission spectrum indicate that the fluorescence property of CdTe quantum dots has been significantly improved after decorating CdTe quantum dots on the surface of graphene. Furthermore graphene/CdTe quantum dots composites were used to quantitative analysis clenbuterol base on the formation of hydrogen bond between clenbuterol and graphene/CdTe quantum dots composites. The fluorescence of graphene/CdTe quantum dots composites can be efficiently quenched by clenbuterol, and there is a good line relationship between the fluorescence intensity decreasing (F_0/F) and the concentration of clenbuterol in the range from 7.22~108.30 $\mu mol \cdot L^{-1}$ with the detection limit of 4 $\mu mol \cdot L^{-1}$.

Keywords: Graphene/CdTe composites; synthesis; characterization; fluorescent probe

0 Introduction

Quantum dots (QDs), a brand class of fluorescent nanoprobes with advantageous of tunable optoelectronic properties, high quantum yield, long-term photostability, narrow emission and independent of the excitation wavelength[1-2], have attracted considerable attention for the development of sensitive and selective fluorescence sensors in recent ten years[3-9]. However, some characteristic limitations, such as particle growth, photoinduced decomposition and conjugate aggregation[10], are effectiveness for applications. Graphene, as a highly transparent semimetal, has unique and interesting electronic, mechanical and thermal properties, which has almost constant absorbance over the visible range and does not exhibit any plasmonic signature in the visible range[11]. References[12-16] have reported that quantum dots (CdS, CdSe and CdTe) can grow over graphene during the synthesis procedure, which can achieve a good electronic contact with the CdTe quantum dots[17], and their photo physical and chemical properties have shown tremendous potential for different applications. In recent years, CdTe quantum dots decorated on the graphene has also become a hot issue to develop sensitive and selective electrochemical sensors [18-21]. However, single-layer graphene or graphene oxide can quench the fluorescence intensity of quantum dots[22-23], which may limit its application as a probe.

Clenbuterol (CLB), called β_2-adrenoceptor agonist, is mainly used in asthma and depression[24]. In the early 1980s, CLB has been used illegally by farmers to make their pigs leaner[25]. But overuse of clenbuterol will be harmful to human being, because CLB will be kept in the meat and liver of animals for a long time and enter the human body with food[26]. So far there have been more than 1 000 incidents caused by clenbuterol[27]. Therefore, the dosages of clenbuterol used as a growth promoter is strictly limited. Different analytical approaches have been developed to quantitative analysis clenbuterol, such as gas chromatography-mass spectrometry (GC-MS) [28], liquid-mass spectrometry (LC-MS) [29-30], high-performance liquid chromatography (HPLC)[31], enzyme-linked immunosorbent assay (ELISA)[32-33], capillary immunochromatographic assay[34], surface-enhanced raman spectroscopy (SERS)[35], molecular imprinting[36], electrochemical methods[37], fluorescence resonance energy transfer (FRET)[38], *etc*. But these methods have disadvantages, such as needs complex sample pre-treatment process, requires specific antibody against the analyte, time-consuming and complicated, relatively expensive equipment, advanced technical expertise, extensive sample preparations and time-consuming, prevent it from developing and expanding its application. Therefore it is quite necessary to develop other sensitive methods for clenbuterol determination. Fluorescence quenching method, which has a linear relationship between decreasing of fluorescence emission intensity of nano-materials and concentration of quencher, has gained vast attention. Cao[39] has reported a fluorescence quenching method for clenbuterol determination in pork mince, but before detection clenbuterol should be derivatized by a diazotization reaction, which is a little complex for real sample analysis.

In this work, thiol graphene was used as stabilizer, and prone to adsorb CdTe onto its surface due to the formation of Cd-S bonds between sulfhydryl of graphene and CdTe quantum dots. The reaction between graphene and CdTe quantum dots was similar to the reaction between thiohydracrylic acid and CdTe quantum dots. Also the X-ray photoelectron spectroscopy (XPS) investigation show that thiol graphene has been reduced due to excessive dose of sodium borohydride used, this may the reason why as-prepared graphene/CdTe quantum dots composites maintain its good fluorescence properties. Furthermore, as prepared graphene/CdTe quantum dots composites has been used as fluorescent probe for quantitative analysis of clenbuterol. To the best of our knowledge, the detection of clenbuterol based on the fluorescence quenching of graphene/CdTe quantum dots composite has rarely been reported, which would be a suitable candidate for quantitative analysis of clenbuterol.

1　Experimental

1.1　Reagents and apparatus

Clenbuterol hydrochloric acid was obtained from Beijing Chemical Company. 3-mercaptopropyl acid (MPA) (99+%), tellurium powder (~200 mesh, 99.8%), CdCl$_2$ (99+%), NaBH$_4$ (99%) were from Aldrich Chemical Co. Thiol graphene was purchased from Suzhou Heng Ke graphene Technology Co., Ltd. (China). All other agents were of analytical reagent grade and used as received. Water used throughout was doubly distilled water (>18 MΩ·cm).

The transmission electron micrographs were recorded with a Tecnai G220 electron microscope (Filament voltage is 3.8 kV, high voltage of TEM is 220 kV). The fluorescence spectra were obtained by using F-280 spectrofluorophotometer equipped with a xenon lamp and 1 cm quartz carrier. UV absorption spectra were measured on shimadzu UV-2550 UV-visible spectrometer. Fluorescence decay curve was obtained using FLS 920 transient steady state fluorescence spectrometer (Edinburgh Instruments). The XPS spectra were recorded with a Thermos Scientific K-Alpha.

1.2　Preparation of graphene/CdTe quantum dots composites

The graphene/CdTe quantum dots was prepared according to a method as Gao and Sun have reported[40-41]. In brief, freshly prepared NaHTe solution, produced by reaction of NaBH$_4$ solution with tellurium powder at a molar ratio of 2:1, was added to nitrogen-saturated 100 mL 1.25 mmol·L^{-1} CdCl$_2$ aqueous solution at pH= 11.4 in the presence of 30 μL MPA and 1 mg thiol graphene as a stabilizing agent. The resulting mixture was then subjected to refluxing to control the size of the CdTe nanocrystals on the graphene/CdTe quantum dots. Finally, products with different fluorescence wavelength were synthesized under different refluxing conditions separately. Then this graphene/CdTe quantum dots composite solution was concentrated by adding acetone, and washed by using ethanol for three times, then dried at 80 ℃, orange crystal was obtained. After weighed, the crystal was dissolved in 5 mL of distilled water (50 mg·mL^{-1}) and stored at 0~4 ℃.

1.3　Quantitative analysis of clenbuterol with graphene/CdTe quantum dots composites

10 μL of clenbuterol was added into 0.1 mL of graphene/CdTe quantum dots composites solution (10 mg·mL^{-1}), and then this solution was end up diluted to 2 mL with distilled water (the concentration of graphene/CdTe quantum dots composites was 0.5 mg·mL^{-1}, the pH=7.0). The fluorescence emission spectrum of this final solution was taken after incubated for 30 min at room temperature. The excitation wavelength was 380 nm and the slit widths of excitation and emission were both 5.0 nm.

2　Results and discussions

2.1　Characterization of graphene quantum dots

In this work, thiol graphene was used as stabilizer, which was prone to adsorb CdTe onto its surface due to the formation of Cd-S bonds between sulfhydryl of graphene and CdTe quantum dots, which was similar to the reaction between thiohydracrylic acid and CdTe quantum dots.

The morphologies of graphene/CdTe composites was characterized using TEM, as shown in Fig.1a, the as-prepared graphene/CdTe composites has plate-like structures. The existence of the lattice plans in the HRTEM image of the particles (Fig.1b) indicates that the particles of CdTe quantum dots are well scattered on the surface of graphene, and the CdTe quantum dots are nearly spherical in shape with an average size of 2.7 nm, and the inter-planer distance of crystalline lattice plane of CdTe quantum dots is 0.38 nm which corresponds to the (111) diffraction plane of CdTe.

Selected graphene/CdTe composites was also characterized by the absorbance and fluorescence spectra. As shown in Fig.2a, the strong absorbance peaks at 231 nm is corresponded to π-π* transition of C=C bond of graphene, and the absorption peaks at 480 nm is corresponded to CdTe quantum dots, and the corresponding emission peaks are at 564 nm (the excitation wavelength is at 380 nm). Compared with the absorbance spectrum of bare CdTe quantum dots
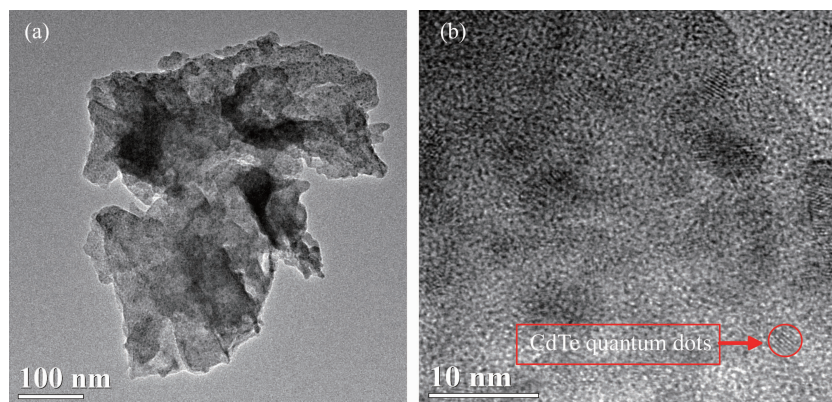
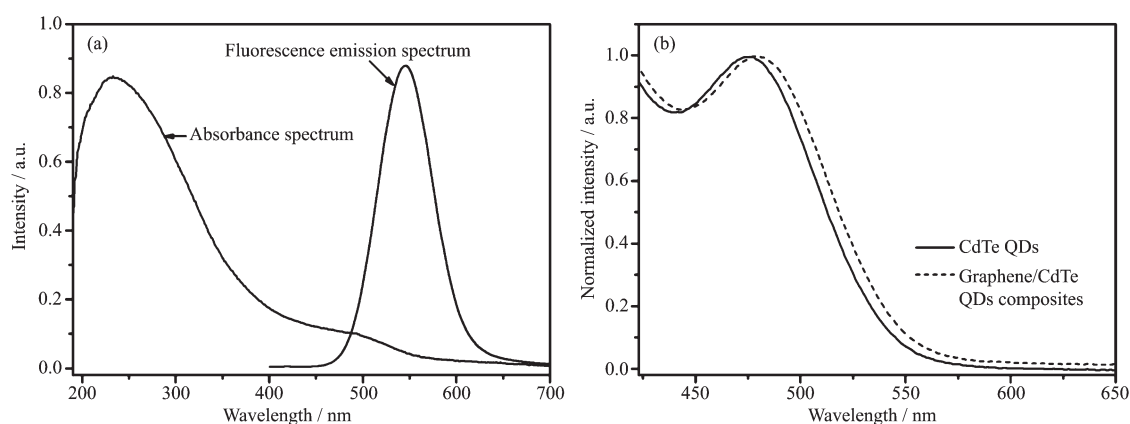Fig.1　TEM images of graphene/CdTe composites

Fig.2　Absorbance spectrum and fluorescence emission spectrum of graphene/CdTe composites (a);
Absorbance spectra of graphene/CdTe composites compared with that of bare CdTe quantum dots (b)

(synthesized in same condition as a controlled experiment), the maximum absorbance peak of graphene/CdTe composites has red shifted a little (about 4 nm).

　　Similar results could be concluded from Fig.3a, the maximum fluorescence emission peak of graphene/CdTe composites has a red shift (about 7 nm) compared with that of bare CdTe quantum dots. Both the red shift of absorbance spectrum and fluorescence spectrum is due to dense CdTe quantum dots decorating on the surface of graphene, which could be confirmed by Fig. 1b. Furthermore the fluorescence decay curves of graphene/CdTe composites with that of bare CdTe quantum dots are shown in Fig.3b. The emission kinetics of CdTe quantum dots fitted multiexponentially with time constants of τ_1=26.8 ns (62.4%), τ_2= 8.7 ns (31.6%) and τ_3=2.2 ns (6.1%), while the emission kinetics of graphene/CdTe composites fitted multiexponentially with time constants of τ_1=2.4 ns

(8.3%), τ_2=11.9 ns (35.2%) and τ_3=45.5 ns (56.5%), respectively. The average fluorescence decay time of CdTe quantum dots (τ_0=20 ns) and graphene/CdTe composites (τ_0=30.1 ns) were calculated by weighted average method. For bare CdTe quantum dots, multi-exponential dynamics arises from Te related surface traps. Since there is an energetic heterogeneity of traps states, it leads to a trap state energy distribution[42-43]. Compared to that of bare CdTe quantum dots, Te related surface traps of graphene/CdTe composites decreases and the redox energy level of Te traps shifts to lower energies, so the average fluorescence decay times of graphene/CdTe composites increased[44]. This may be the reason why the fluorescence intensity of graphene/CdTe composites increased nearly 5 folds compared with bare CdTe quantum dots (Fig.3a).

　　Chemical bonding in graphene and graphene/CdTe composites were analyzed by using the XPS spectra (Fig.4). Compared to the characteristic peaks
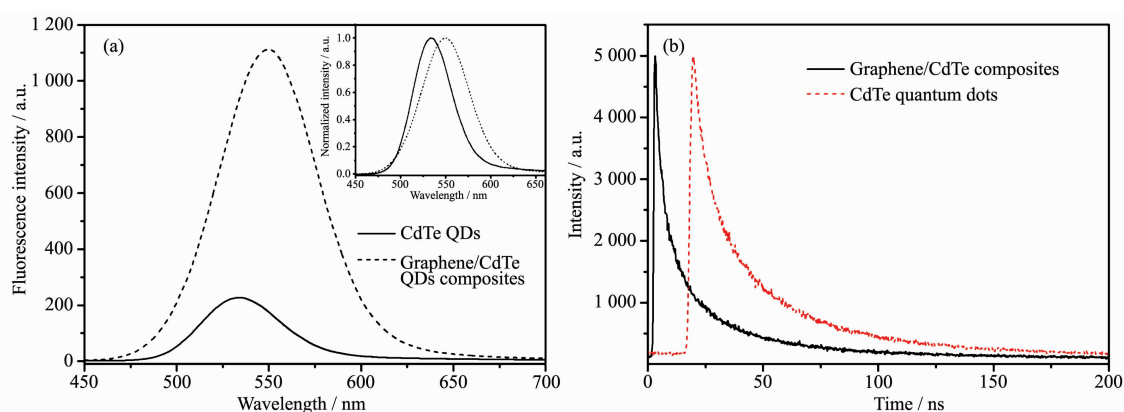
Fig.3　Absorbance spectrum and fluorescence emission spectrum of graphene/CdTe composites (a);
Fluorescence decay curve of CdTe quantum dots and graphene/CdTe composites (b)

of graphene, there not only has characteristic peaks corresponding to C1s, S2p and O1s, but also has characteristic peaks corresponding to Cd3d and Te3d in XPS spectrum of graphene/CdTe composites, which confirms the presence of Cd and Te in graphene/CdTe composites. Deconvoluted high resolution XPS spectra for Cd3d, and Te3d are shown in Fig.5. The appeara-

Fig.4　XPS spectra of graphene and graphene/CdTe composites

nce of a Cd3$d_{5/2}$ peak at 405.1 eV, a Cd3$d_{3/2}$ peak at 411.7 eV, a Te3$d_{5/2}$ peak at 572.7 eV, a Te3$d_{3/2}$ peak at 583.1 eV, and the binding energies of CdS are at 407.6 and 414.4 eV (Fig.5a), all this confirm that CdTe was decorated on the surface of graphene. Furthermore, in addition to the two main Te peaks (Fig.5b), there are two peaks at higher binding energies (576.2 and 586.6 eV), which are corresponded to Te (Ⅳ) oxide[45-46]. Thus, the unpassivated surface Te is prone to the oxidation process, which can create surface defect states.

The S2p spectrum was also studied by means of XPS-peak-differentiation-imitating analysis (Fig.6). For S2p spectrum of graphene, three fitting peaks at 168.5, 169.8 and 172.0 eV (Fig.6a), which are corresponded to the characteristic peaks of S2p[47] and inorganic sulfur[48], indicates the existence of mercapto-function group on the surface of graphene. While for S2p spectrum of graphene/CdTe composites, three
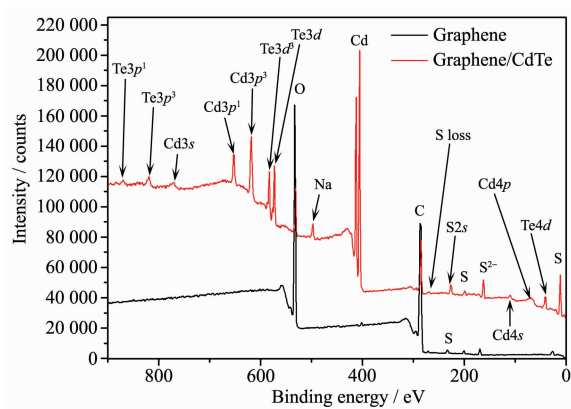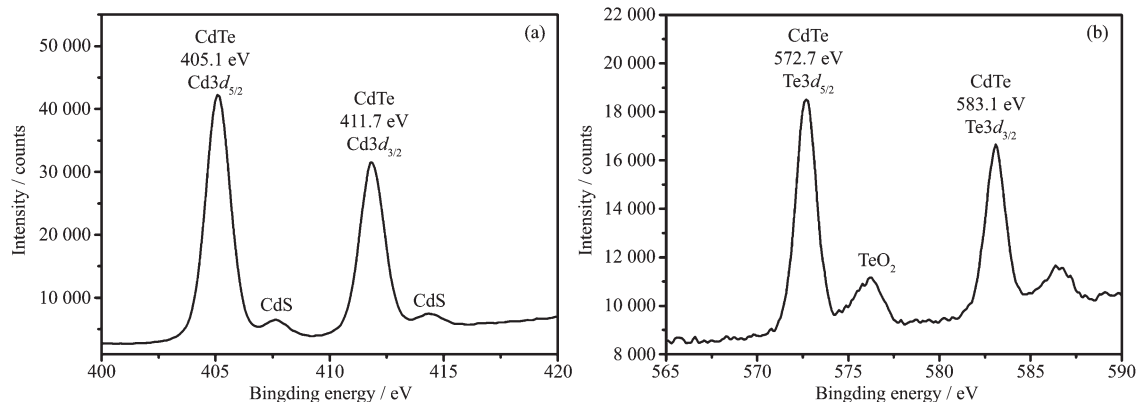

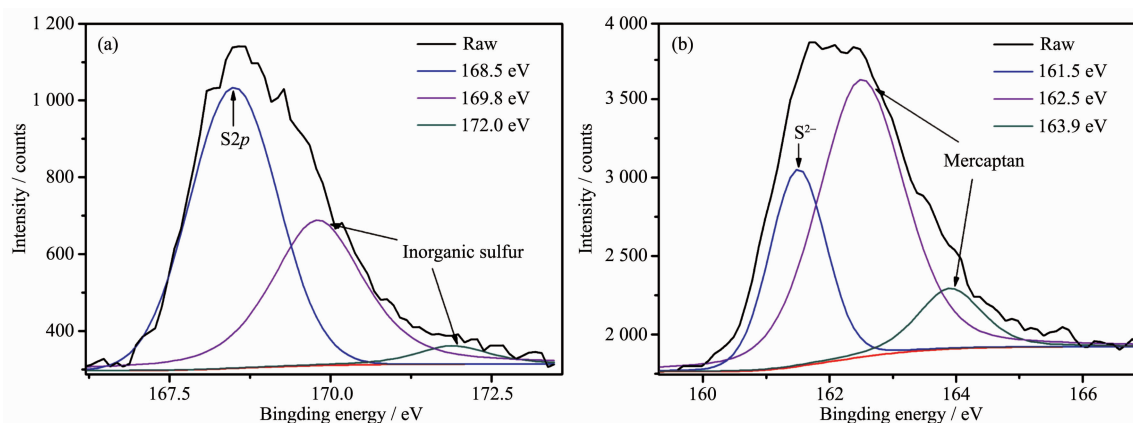Fig.5　Cd (a) and Te (b) XPS spectrum of graphene/CdTe composites

Fig.6   S2p spectrum of graphene (a) and graphene/CdTe composites (b), which were studied by means
of XPS-peak-differentiation-imitating analysis

fitting peaks at 161.5, 162.5 and 163.9 eV (Fig.6b), which are corresponded to the characteristic peaks of S^{2-} and mercaptan[48], indicates the existence of CdS and mercaptan group on the surface of graphene. All this also indicates that MPA modified CdTe quantum dots has been successfully decorated on the surface of graphene.

The C1s and O1s spectrum were studied by means of XPS-peak-differentiation-imitating analysis (Fig.7 and 8). For C1s spectrum of graphene, there are four fitting peaks at 284.8, 286.9, 288.1 and 289.3 eV (Fig.7a), which are corresponded to the characteristic peaks of C=C (graphitic carbon), C-O, C=O and O=C-O, while for C1s spectrum of graphene/CdTe composites, there are six fitting peaks at 284.5, 285.9, 286.8, 287.8, 288.3 and 288.6 eV (Fig.7b), which are corresponded to the characteristic peaks of C=C (graphitic carbon), C-OH, C-O, C-O-C, C=O and O=C-

O[49-50]. For O1s spectrum of graphene, there are four fitting peaks at 533.3, 532.7, 535.2 and 531.9 eV (Fig.8a), which are corresponded to the characteristic peaks of C-O, C-O-H, C=O and O-S, while for O1s spectrum of graphene/CdTe composites, there are three fitting peaks at 531.6, 532.0 and 532.6 eV (Fig. 8b), which are corresponded to the characteristic peaks of surface chemical adsorption of oxygen, CdO and TeO. All these indicate that oxygen-containing functional group has decreased significantly, and graphene with 1-octadecanethiol has been reduced due to excessive dose of sodium borohydride. And results also indicate that there are carboxyl and hydroxyl groups on surface of graphene/CdTe composites, which are from MPA, so it has good hydrophilicity. Above all, graphene/CdTe composites have been successfully synthesized.
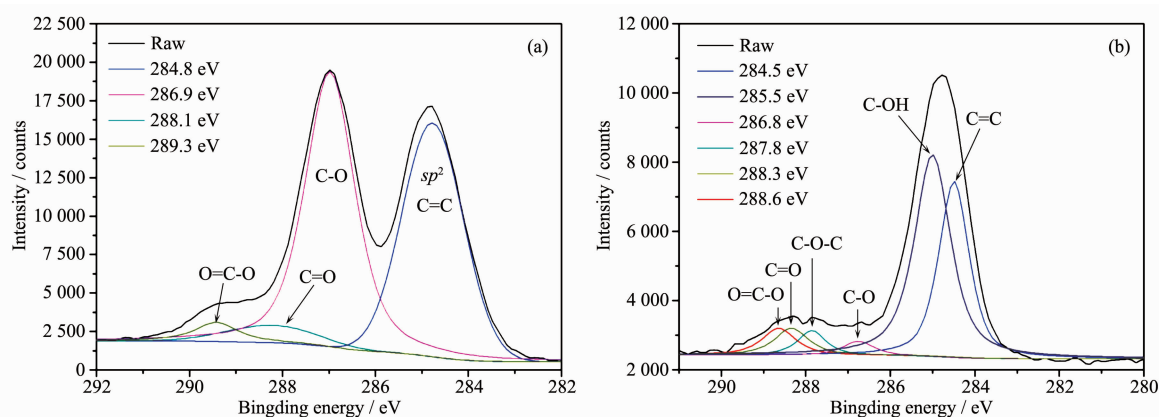

Fig.7   C1s spectrum of graphene (a) and graphene/CdTe composites (b), which were studied by
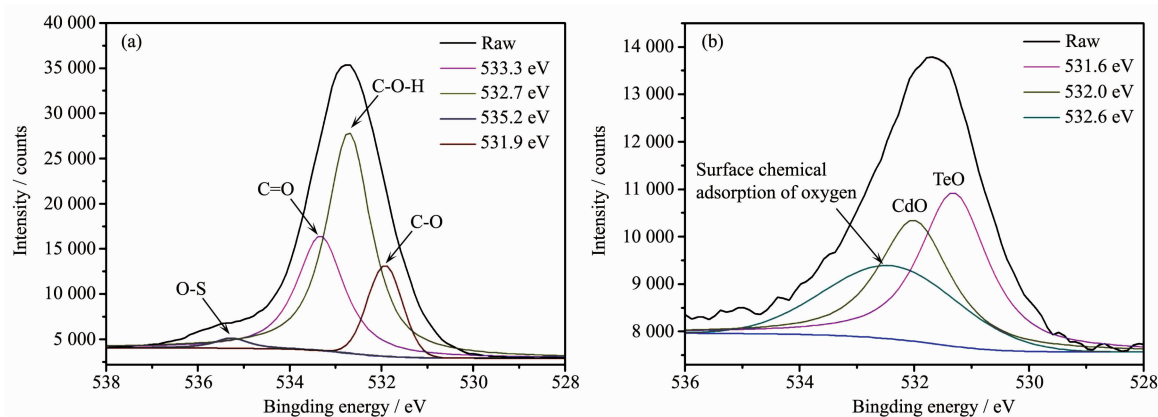means of XPS-peak-differentiation-imitating analysis

Fig.8　O1s spectrum of graphene (a) and graphene/CdTe composites (b), which were studied by means of XPS-peak-differentiation-imitating analysis

2.2　Quantitative analysis of clenbuterol by graphene/CdTe composites

When clenbuterol was added into the graphene/CdTe composites solution, the fluorescence of graphene/CdTe composites was remarkably quenched and 1.26 mmol·L^{-1} clenbuterol can produce a quenching extent of 80%. The mechanism is similar to that we have reported[51]. In this system, there are -OH and -NH- in each clenbuterol molecule, and carboxyl groups on the surface of graphene/CdTe composites. The oxygen atoms on the surface of the carboxyl groups and -NH- groups both have strong electronegativity, and a complex of graphene/CdTe composites with clenbuterol is formed through hydrogen bonding (as shown in Fig.9).

In order to develop and apply this method further, the effect of pH and incubation time on this
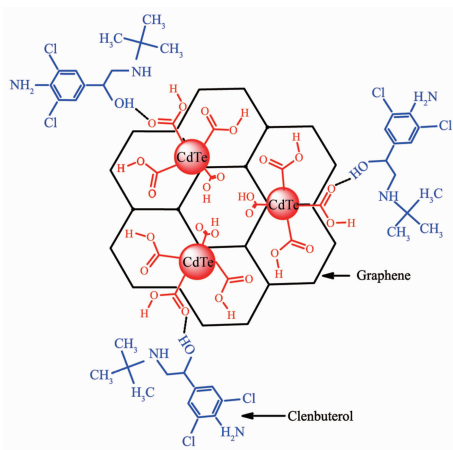

Fig.9　Schematic illustration of the interaction of graphene/CdTe composites with clenbuterol

sensor system was investigated and optimized. Fig.10a shows that the F_0/F of this sensor system increases with the decrease of pH value, and reached a maximum value at 5.0. But the stability of CdTe quantum dots is most stable in neutral and base solution[52], so pH=7.0 was selected for further application. Fig.10b shows that the F_0/F of this sensor system decreased a little first and then increased with incubation time (from 0 to 33 min), and the variation of F_0/F could be negligible after 30 min, so the incubation time of 30 min was selected for further application. And room temperature was selected for convenience.

Under optimal experimental conditions, various concentrations of clenbuterol solution (7.22~108.30 μmol·L^{-1}) were added into graphene/CdTe composites solution. Fluorescence spectra were measured (shown in Fig.11), and there is a good linear relationship between the F_0/F and the concentration of clenbuterol (F_0 and F were the fluorescence intensity of graphene/CdTe composites in the absence and presence of clenbuterol, respectively). The linear regression equation is $F_0/F = 0.032C_{clenbuterol} + 0.79$. The corresponding regression coefficient was 0.998. The equation [53] LOD=$(3.3\sigma/k)$ is used to calculate the limit of detection (LOD), where σ is the standard deviation of the y-intercepts of the regression lines and k is the slope of the calibration graph, so the low detection limit for clenbuterol is 4 μmol·L^{-1}.

Furthermore this quenching method was applied on urine detection. The specificity of this assay was
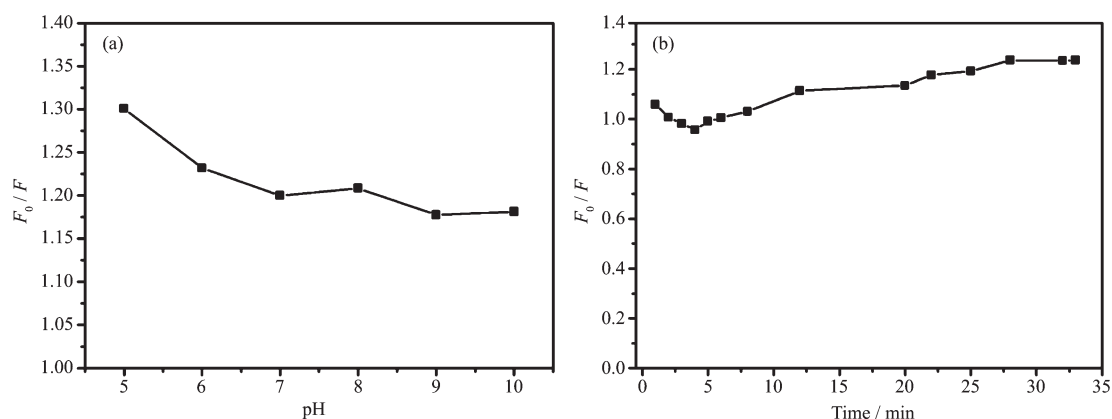
Concentration of graphene/CdTe composites and clenbuterol are 0.5 and 15 μmol·L^{-1}, respectively

Fig.10　Effects of pH and reaction time on the F_0/F of the system (a, b)
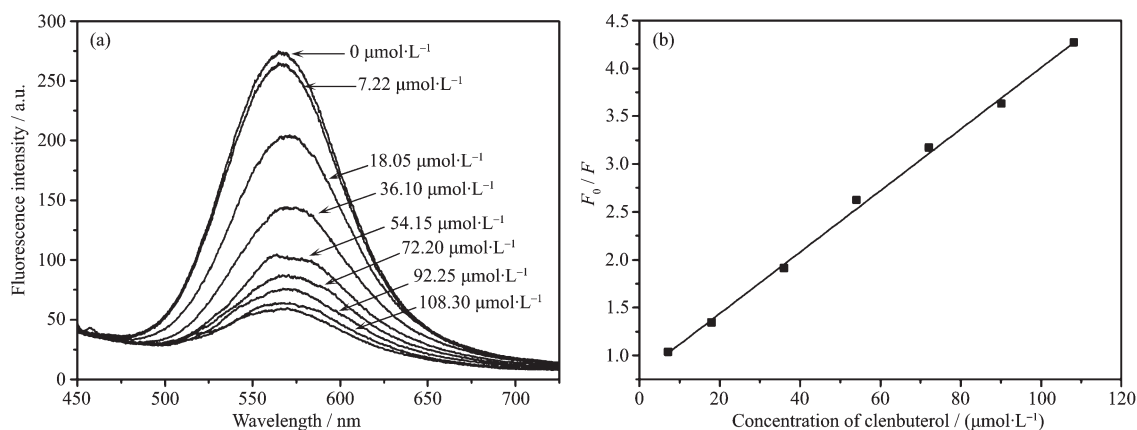
Concentration of graphene/CdTe composites was 0.5 mg·mL^{-1}, and λ_{ex}=380 nm

Fig.11　Clenbuterol concentration-dependent fluorescence emission of graphene/CdTe composites and
the variation of F_0/F as a function of clenbuterol

evaluated before practical application. Effects of various substances such as clenbuterol (CLB), salbutamol (Salb), ractopamine (Ract), BSA, glucose, sucrose, urea, Na$^+$ and K$^+$ on the F_0/F of this sensor system under the optimum conditions were shown in Fig.12. No obvious change of the fluorescence intensity was observed upon the addition of each compound. It demonstrates that this method exhibits good selectivity for the detection of clenbuterol.

To estimate the practical application potential of this fluorescent immunosensor, relative standard deviation (RSD) and recovery test of clenbuterol in human urine was evaluated by determination of the recovery of spiked clenbuterol in five diluted human urea samples (1%). As shown in Table 1, 10, 50 and 100 μmol·L^{-1} of clenbuterol were added into water

and urine samples, respectively. The recovery of clenbuterol is ranged from 98.4% to 100.3%, and the RSD is ranged from 1.8% to 3.1% . These results showed that the graphene/CdTe composites had great potential for quantitative analysis of clenbuterol in

Table 1　Results of detection of clenbuterol in urine

	Cclenbuterol / (μmol·L^{-1})		Recovery
	Added	Found[a]	
Distilled water	10	10.03±0.18	100.3%
	50	49.93±1.31	99.86%
	100	99.91±2.14	99.91%
Urine	0	0	ND
	10	9.84±0.14	98.4%
	50	49.76±1.52	99.52%
	100	98.89±2.35	98.89%

[a]Mean of three experiments; ND: not detected.
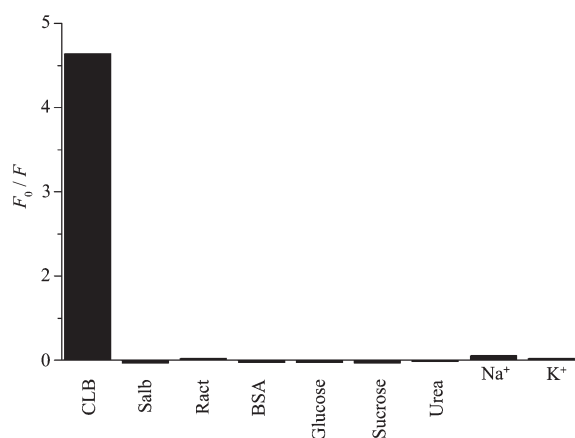
Concentration of graphene/CdTe composites was 0.5 mg·mL^{-1}, the concentration of CLB, Salb and Ract was 0.1 mmol·L^{-1}, the concentration of other substances were 1 mg·mL^{-1}, λ_{ex}=380 nm

Fig.12　Effects of various substances such as clenbuterol (CLB), salbutamol (Salb), ractopamine (Ract), BSA, glucose, sucrose, urea, Na$^+$ and K$^+$ on the F_0/F of this sensor system under the optimum conditions

urine samples.

3　Conclusions

Above all, graphene/CdTe quantum dots composite was successfully synthesized and used as a fluorescent quenching sensor for quantitative analysis of clenbuterol. The as-prepared composite was characterized using TEM, absorption spectrum, fluorescent emission spectrum, fluorescence decay curve and XPS. The proposed fluorescent sensor achieved excellent performance for clenbuterol detection, and the linear relationship between the fluorescence intensity decreasing (F_0/F) and the concentration of clenbuterol in the range from 7.22 ~108.30 μmol·L^{-1} with a detection limit of 4 μmol·L^{-1}. And this method was also applied in the determination of the concentration of clenbuterol in urine. Above all, this fluorescent quenching sensor provides a fairly practical and economical approach, which has great potential to evaluate the exceeding standard of clenbuterol with a fluorimetric detection limit.

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