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SYNTHESIS OF FUNCTIONALIZED CdTe/ZnS NANOPARTICLES AS PROBES FOR NORFLOXACIN FLUORESCENCE DETECTION

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In this study, a functionalized CdTe/ZnS nanoparticles (NPs) were successfully synthesized with thioglycolic acid (TGA) as the capping ligand. The prepared nanoparticles were carefully characterized using XRD, TEM and FTIR spectroscopy. Based on the quenching of the fluorescence intensity of functionalized CdTe/ZnS NPs by norfloxacin, a novel, simple and rapid method for the determination of norfloxacin was proposed. The optimum conditions for norfloxacin detection was studied in detail. The results indicate that the TGA functionalized CdTe/ZnS NPs could act as an excellent probe for norfloxacin fluorescence detection

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Keyword: CdTe, ZnS; Norfloxacin; Fluorescence; Quenching

1. Introduction

Norfloxacin, 1-ethyl-6-fluoro-1,4-dihydro-4-oxo-7-(1- piperazinyl)-3 quinolonecarboxylic acid, is a fluoroquinoline carboxylic acid. It has effectives against gram-positive and gramnegative bacteria through inhibition of their DNA gyrase [1, 2]. Norfloxacin is used in a wide range of gastrointestinal, urinary, respiratory tract, ocular and skin infections. It is also used in patients with intra-abdominal infections in combination with antianaerobic agents [3, 4]. Therefore, the widespread use of norfloxacin and the need for clinical and pharmacological study require fast and sensitive analytical methods for its determination.

Till date, there have been a great many techniques reported such as HPLC [5, 6], UV detection [7] and electrochemical analysis [8-11]. However, these techniques exist deficiencies include: time consuming, expensive reagents and tedious sample pretreatment. To overcome these disadvantages, there is a need for rapid, simple and low-cost methods for the efficient determination of drugs. In contrast, luminescence techniques provide a very elegant method in analytical chemistry. Very few studies involving luminescence determination of norfloxacin have been reported recently [12, 13]. Therefore, novel techniques for the determination of norfloxacin are still needed to be developed.

Luminescent semiconductor NPs hold immense promise to use as fluorescence probes. Semiconductor NPs present a series of excellent optical and chemical properties, such as long-term photostability, broad excitation spectrum, narrow/symmetric emission spectrum, and readily tunable spectra [11, 14-16]. A great deal of studies on various semiconductor NPs used as fluorescence probes have been reported in the past decades, such as CdTe, CdS, ZnS, and CdSe, and excellent results have also been achieved [17-20].

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In the present work, a simple and rapid method was proposed based on the quenching of fluorescence intensity of thioglycolic acid (TGA) capped CdTe/ZnS NPs in the presence of norfloxacin in aqueous solution. CdTe/ZnS NPs were synthesized by a hydrothermal method and TGA was used as the stabilizer. Under optimum conditions, fluorescence intensity decreased with the concentration increase of norfloxacin. Successful results of the determination of norfloxacin in real samples were also obtained.

2. Experimental

2.1 Materials

Sodium borohydride (96 %), $Na_2S{\cdot}9H_2O$ (analytical purity), tellurium powder (99.999 %), $CdCl_2{\cdot}2.5H_2O$ (analytical purity), thioglycolic acid (TGA), rhodamine B, norfloxacin and $ZnSO_4{\cdot}7H_2O$ were acquired from Sigma and all of the reagents mentioned above were used without any further purification. Phosphate buffer solution (PBS) was prepared by adjusting 0.1 M K_2HPO_4, KH_2PO_4, H_3PO_4 or NaOH. Milli-Q water was used throughout the experiments.

2.2 Synthesis of TGA functionalized CdTe/ZnS NPs

For a typical synthesis of TGA functionalized CdTe NPs, $CdCl_2{\cdot}2.5H_2O$ (91.3 mg, 0.4 mM) and TGA (0.1 mL) were dissolved in water (95 mL), and the pH of the solution was adjusted to about 9 by stepwise addition of 1.0 M NaOH solution. Then, the solution was saturated with N_2 for 20–30 min. After that, the fresh oxygen-free NaHTe solution prepared previously was quickly injected into the above solution under vigorous stirring. After boiling for 10 min in an oil bath, the solution was transferred to a water bath and maintained at 60 °C for 1 h. Consequently, TGA functionalized CdTe NPs were obtained, where the molar ratio of Cd^{2+}/Te^{2-}/L-cysteine was 1 : 0.5 : 2.5. For a typical synthesis of TGA functionalized CdTe/ZnS NPs, as-prepared CdTe sample was dispersed in 80 mL aqueous solution (pH = 9) that contained $ZnSO_4$ (230 mg, 0.8 mmol) and TGA (0.1 mL). The mixture was then saturated with N_2 for about 20 min beforehand. Subsequently, Na_2S solution (20 mL) was added into the above solution dropwise under vigorous stirring. The molar ratio of Zn^{2+}/S^{2-} and Cd^{2+}/Zn^{2+} was controlled to 1 : 1 and 1 : 2, respectively. Finally, the mixture was boiled for 7–8 min and refluxed in a water bath (60 °C) for 1.5 h.

2.3 Characterization

The morphology of the samples was analyzed by a JEM-2010F transmission electron microscope (TEM). The surface functional groups present on the samples were analyzed by Fourier transform infrared spectroscopy (FTIR, Nicolet iS5, Thermo Scientific, USA). X-ray diffraction (XRD) patterns were carried out using X'Pert Philips diffractometer with Cu anode. The excitation wavelength was 315 nm. The optical properties of the samples were analyzed by UV-vis diffuse reflectance spectroscopy (UV-vis DRS) using a UV-vis spectrophotometer (Cary-500, Varian Co.)

2.4 Determination of Norfloxacin with CdTe/ZnS Fluorescence Probes

The detection procedures are as follows: in a set of 25 mL calibrated brown volumetric flasks, 300 μL of the as-prepared TGA functionalized CdTe/ZnS NPs solution and a series of different concentrations of norfloxacin standard solutions were added. The mixtures were diluted to the volume with PBS (pH=7.5) solution. The fluorescence spectra were recorded at an excitation wavelength of 400 nm with excitation and emission slits width of 5 nm. The photomultiplier tube voltage was set at 800 V.

3. Results and discussion

Fig. 1 shows the morphology of prepared CdTe/ZnS NPs using TEM technique. As shown in Figure 1A, the shape of the CdTe/ZnS NPs was close to spherical and well distributed. Under

high resolution TEM characterization (Figure 1B), it could be found the average size of the CdTe/ZnS NPs was about 2.8 nm.

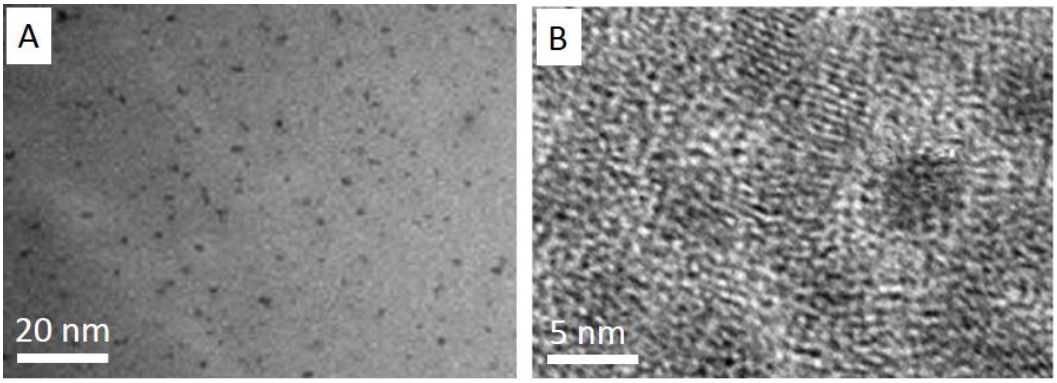

Fig. 1. TEM images of CdTe/ZnS NPs.

Fig. 2A shows the powder XRD analysis results of CdTe NPs and CdTe/ZnS NPs prepared during the synthesis process.The characteristic peaks located at 24.77°, 41.15° and 46.10° for CdTe are corresponding to the zinc blend planes of CdTe NPs sample. The peaks at 26.51°, 43.96° and 52.13° observed in CdTe/ZnS NPs sample also corresponding to the CdTe. After the growth of ZnS, these peak position shifted to higher angles towards the positions of ZnS cubic structures peaks.

Figure 2B shows the UV-vis absorption spectrum and fluorescence spectrum of CdTe/ZnS NPs. It can be seen that the CdTe/ZnSfluorescence probes have a wide range of absorption with a shoulder centers at about 570 nm. The emission spectrum of CdTe/ZnS NPs is narrow and symmetric with the maximum emission wavelength at about 600 nm.The quantum yields of CdTe/ZnS NPs were estimated to be 37% using rhodamine B as reference, in comparison with 31% of CdTe NPs, indicating the surface defects of CdTe NPs were improved by growth of ZnS.

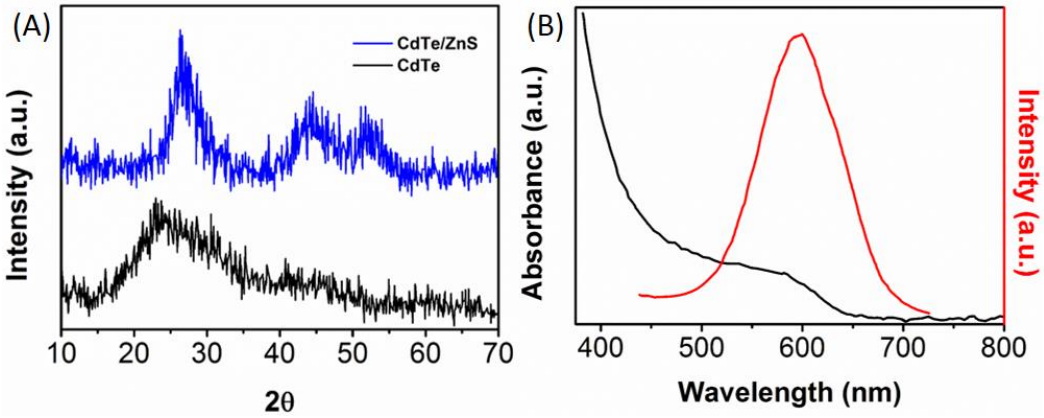

Fig. 2. (A) XRD patterns of CdTe NPs and CdTe/ZnS NPs. (B) UV-vis absorption spectrum and fluorescence emission spectrum of CdTe/ZnS NPs

Fig. 3 shows the FTIR spectra of TGA and TGA functionalized CdTe/ZnS NPs. It can be seen that the TGA presents various peaks. The peak located at 1552–1850 can be attributed to the vibration of C=O. The peak at 1205–1290 cm^{-1} can be assigned to the vibration of C–O bonds. The peak at 1420–1460 cm^{-1} can be assigned to the vibration of COOH. The peak at 3500-3000 cm^{-1} is due to the vibration of OH and COOH groups. The peak at 600–800 cm^{-1} indicates the C–S group. Most of these peaks can be found at TGA functionalized CdTe/ZnS NPs, which indicating the coexistence of carboxyl and carbonyl groups on the surface of the CdTe/ZnS NPs. However,

the peak related to the C–S group was missing in the spectrum of CdTe/ZnS NPs. The possible reason for this phenomenon is due to covalent bonding interactions between thiols and the surface of CdTe/ZnS.

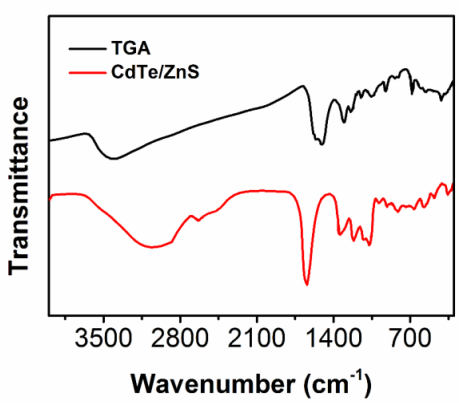

Fig. 3. FTIR spectra of TGA and CdTe/ZnS NPs.

pH and reaction time are two most important factors that influence the fluorescence intensity. It has been reported that the nanoparticles are pH sensitive materials which could lead to different fluorescence quantum yield at different pH conditions. Figure 4A shows the change in the fluorescence intensities of CdTe/ZnS NPs with the pH from 3.00 to 11.00 in the presence of 2 μm norfloxacin. It can be observed that the pH value can have an impact on the reaction process. pH of 7 shows the best intensity results. Therefore, pH 7 was chosen as optimum pH condition in this study. The effect of the reaction time on the fluorescence intensity of the system was also tested. As shown in Figure 4B, a stable fluorescence intensity was obtained after reacting for 90 min. Hence, the fluorescence intensity was recorded after the system had reacted for 90 min.

Under the optimal conditions, the CdTe/ZnS NPs were employed for quantifying norfloxacin with different concentrations based on FL quenching of CdTe/ZnS NPs.

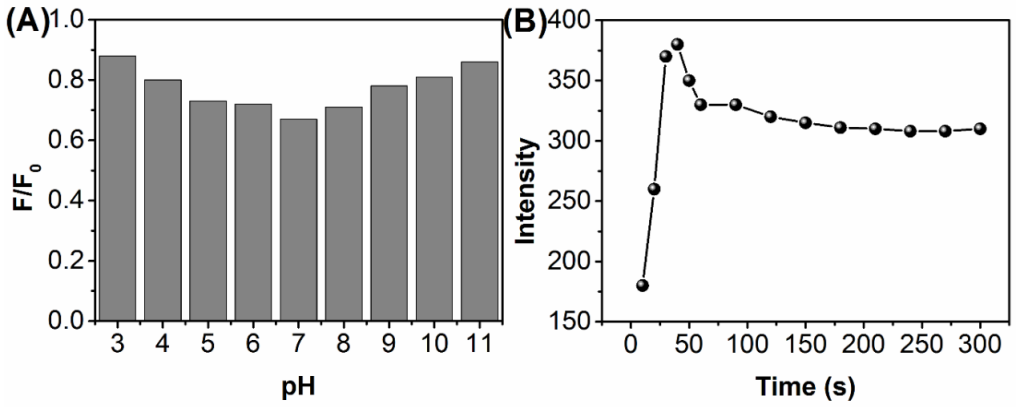

Fig. 4. (A) Effect of pH on the fluorescence intensity of CdTe/ZnS NPs. (B) Effect of reaction time on the fluorescence intensity of the CdTe/ZnS

Figure 5A shows the effect of the norfloxacin on the fluorescence emission of the CdTe/ZnS NPs. It can be clearly found that the fluorescence intensity of CdTe/ZnS NPs with different concentrations of norfloxacin was significantly reduced in the increasing concentrations of norfloxacin.These results demonstrate that the prepared CdTe/ZnS NPs provide a suitable basis for the development of a sensitive norfloxacinprobe.

The linear calibration equation and limit of detection for norfloxacin were collected based on above results. Figure 5B shows the linear fitting regards concentrations of Norfloxacin and

fluorescence intensity. The relative fluorescence intensity ($\Delta F = F_0/F$) of CdTe/ZnS NPs increased linearly in the concentration range from 2 to 1400 μm for norfloxacin with the correlation coefficient of 0.99.Stern–Volmer equation was used for describing the quenching effect of the norfloxacin.

$$F0/F = 1 + KsvC$$

Where F_0 and F are the fluorescence intensities in the absence and presence of quencher concentration solution, respectively. C is the concentration of quencher, and Ksv is the Stern–Volmer quenching constant. From the calibration curve, the following equation was established for norfloxacin: $F_0/F = 1.05881 + 0.00101C$. The detection limit ($3\sigma/k$) is 0.022 μM, in which σ is the standard deviation of blank measurements (n = 10) and k is the slope of calibration of the calibration line.

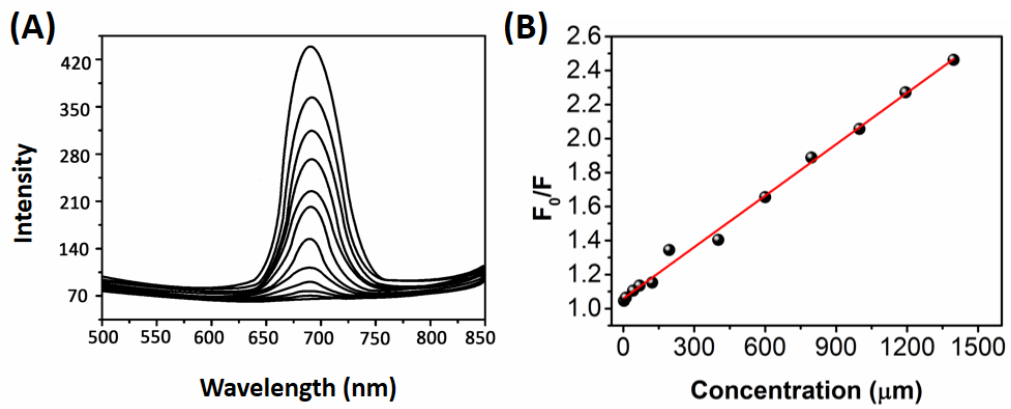

Fig. 5. (A) Fluorescence emission spectra of CdTe/ZnS NPs in the absence and presence of norfloxacin and presence of norfloxacin in concentrations of 5, 80, 200, 400, 600, 800, 1000, 1200, 1300 and 1400 μM. (B) Linear curve of the relative fluorescence intensity (F_0/F) versus the concentrations of norfloxacin.

The prepared CdTe/ZnS NPs probes were also used for real applications. Pharmaceutical formulations were used as real sample for testing the properties of the CdTe/ZnS NPs. UV detection was used as reference. The experiment results were listed in Table 1. It can be seen from the table, the detection of norfloxacin using CdTe/ZnS NPs probe is much accurate than that of UV detection method. Therefore, the CdTe/ZnS NPs are effective fluorescence probes for practical norfloxacin detection.

Table 1.Recovery of norfloxacin in capsules sample at different concentration levels.

Sample	Concentration (μM)	Found		Recovery (%)		RSD (%)	
		FL	UV	FL	UV	FL	UV
1	20	19.877	18.565	99.39	92.83	2.33	1.28
2	40	40.587	40.655	101.47	101.64	1.98	1.56
3	60	59.874	63.212	99.79	105.35	1.58	2.01

4. Conclusion

In summary, our proposed a simple chemical method for synthesizing CdTe/ZnS NPs. A series characterizations were showed the successful formation of composite material. The prepared CdTe/ZnS NPs were then used as fluorescence probes for norfloxacin detection. The results showed this method able to detect the target molecules in a wide concentration range with low detection limit.

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