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RESEARCH PAPER

L- and D-cysteine Functionalized CdS Quantum Dots as Nanosensors for Detection of L-morphine and D-methamphetamine

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ABSTRACT

A new method in differentiation of chiral molecules is reported based on the fluorescence quenching of functionalized CdS quantum dots (CdS-QDs) as nanosensor by differing in the chirality of functionalization species. The chemically functionalized CdS-QDs with strong yellow emission were prepared using chiral L-cysteine (L-Cyst) and D-cysteine (D-Cyst) molecules. Then, the functionalized CdS-QDs were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray (EDX) analysis, photoluminescence (PL), ultraviolet-visible (UV-Vis), and Fourier transform infrared (FT-IR) spectroscopies. The prepared L- and D-cysteine functionalized CdS-QDs were exploited as fluorescence probes for detection and determination of L-morphine and D-methamphetamine. It was found that the fluorescence of D- and L-cysteine functionalized CdS-QDs were efficiently quenched by adding D-methamphetamine and L-morphine to them, respectively. The magnitude of fluorescence quenching depended on the concentration of L-morphine and D-methamphetamine solutions according to the Stern-Volmer equation. So, the functionalized CdS-QDs can be used as simple, quick, cheap, and sensitive nanosensor for practical detection of morphine and methamphetamine.

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INTRODUCTION

In recent years, semiconductor quantum dots (QDs) have been appeared as useful fluorophores due to their tunable emission peaks and size-dependent wavelength as well as good chemical stability [1-5]. These features have provided several technological applications especially in various biological and chemical sensing systems [6-9].

Chirality is one of the most interesting phenomena in the nature and has great importance in molecular recognition which is very useful in chemistry and biology. It has also been known that chirality concept could play a crucial role in nanotechnology [1,11]. The major part of earlier researches in this scope has been devoted to the chiral organic, metal-organic, and biological species [12,13]. The research in the field of chiral inorganic nanostructures is still in the early stage of its growth. The new chiral nanostructures have attracted great attention because of their potential uses in chiral sensing, catalysis, and optical devices [14-16]. There has been some works including optically active metallic gold and silver nanoparticles [17-20] as well as carbon nanotubes [11]. There are a few reports about the applications of chiral semiconducting quantum dots for the analysis of chiral compounds [20-25]. Because of their distinctive photophysical characteristics, chiral QDs may have potential uses in photonics and biochemistry [6,26]. However, the selective interaction of chiral QDs with enantiomers has not

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been well-described so far. Herein, we report the preparation and physicochemical characterization of chiral CdS-QDs using the dextrorotatory (D-) and levorotatory (L-) enantiomers of cysteine. Then, the selectivity of the interaction of L-morphine and D-methamphetamine with the chiral CdS-QDs is discussed. The chiral recognition of the two narcotic drugs, L-morphine and D-methamphetamine, is possible by their enantioselective interaction with the functionalized CdS-QDs. One of the chiral narcotic drugs quenched the fluorescence intensity of the functionalized chiral CdS-QDs more efficient than the other.

MATERIALS AND METHODS

Materials and instrumentation

Cadmium chloride monohydrate and thioacetamide were purchased from Merck chemical company and used without further purification. L- and D-cysteine hydrochloride monohydrate, morphine sulfate, and methamphetamine hydrochloride were purchased from Sigma-Aldrich. Double distilled water was used throughout the experiments. X- ray diffraction (XRD) patterns were obtained on a Philips PW 1730 diffractometer equipped with Cu Kα radiation (λ= 0.154 nm). Transmission electron microscopy (TEM) analyses were carried out on a Zeiss-EM10C instrument with an accelerating voltage of 100 kV. Energy dispersive X-ray analysis was performed by a scanning electron microscope with EDX detector INCA Penta FETx3. Fluorescence analyses were carried out on a Carey Eclipse Fluorescence Spectrophotometer with excitation wavelength of 365 nm. The UV-Vis absorption spectra were recorded on a Perkin Elmer Lambda 20 UV/Vis Spectrophotometer in 1cm quartz cells. The infrared spectra were measured on Perkin-Elmer Spectrum RXI FT-IR spectrometer using KBr pellets.

Synthesis of L- and D-cyst-CdS-QDs

$CdCl_2.H_2O$ (1.2 mmol) and D- or L-cysteine (2.4 mmol) were dissolved in deionized water (60 ml), followed by adjusting the pH value to 10 with 1M NaOH aqueous solution. The solution was degassed by N_2 gas for 0.5 h. Then, thioacetamide (0.6 mmol) was added to the above aqueous solution. The solution was deaerated again by N_2 for 0.5 h and then heated to 100°C for 6 h. The obtained yellow L- or D-cyst-CdS-QDs was precipitated after addition of ethanol, isolated with centrifugation and washed several times with ethanol to remove the impurities. The L- and D-cyst-CdS-QDs were then redispersed and kept in a 100 ml 0.05M Tris HCl buffer solution at pH=7.2.

Emission studies

First, stock aqueous solutions of L-morphine sulfate and D-methamphetamine hydrochloride were prepared. 2 ml of the above prepared L- or D-cyst-CdS-QDs solution was transferred into a quartz cuvette. Then, proper volumes

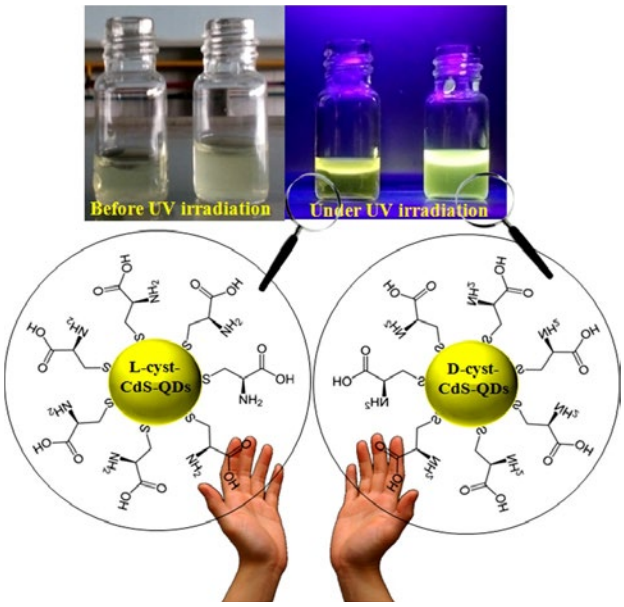

Fig. 1. Representative structures of the L- and D-cyst-CdS-QDs and their emission under UV light.

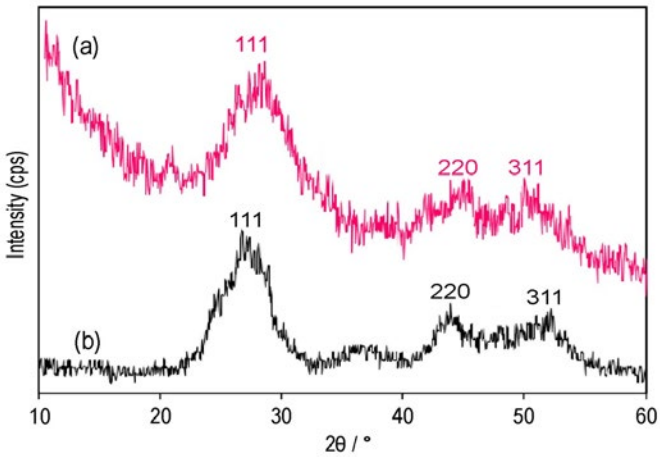

Fig. 2. XRD patterns of (a) L- and (b) D-cyst-CdS-QDs.

of the aqueous solution of L-morphine or D-methamphetamine were added and the fluorescence spectra of L- or D-cyst-CdS-QDs solutions were recorded after each addition.

RESULTS AND DISCUSSION

An overview of the prepared L- and D-cyst-CdS-QDs and their emission under UV light has been outlined in Fig. 1.

Characterization of L- and D-cyst-CdS-QDs

The crystalline structures and phase purities of L- and D-cyst-CdS-QDs were studied by XRD analysis and their patterns presented in Fig. 2. The observed peaks in the XRD patterns of L- and D-cyst-CdS-QDs correspond to the crystal planes of cubic CdS phase (JCPDS reference code 41-1049) [25]. Also, with application of Debye-Scherrer formula [26] for the peak (111), the average crystallite sizes of L- and D-cyst-CdS-QDs were calculated as 3.4 and 3.6 nm, respectively.

The microstructures of the obtained L- and D-cyst-CdS-QDs were analyzed by transmission electron microscopy (TEM) (Fig. 3). As can be seen in the obtained TEM images, due to the aggregation of the quantum dots in solid state, determination of their precise diameters is very difficult. But, the approximate size of the quantum dots is lower than 10 nm.

Energy dispersive X-ray (EDX) analyses of L- and D-cyst-CdS-QDs revealed the presence of Cd and S in the prepared L- and D-cyst-CdS-QDs (Fig. 4).

In the FT-IR spectra of L- and D-cyst-CdS-QDs (Fig. 5), the peaks at 1550-1600 cm^{-1} and 3000-3500 cm^{-1} belong to the stretching vibrations of COO^- and OH groups of cysteine species, respectively. The observed bands in the range of 2900-3000 cm^{-1} can be assigned to the stretching vibrations of C-H bonds. Furthermore, the stretching vibrations of S-H groups are not seen at about 2500 cm^{-1}

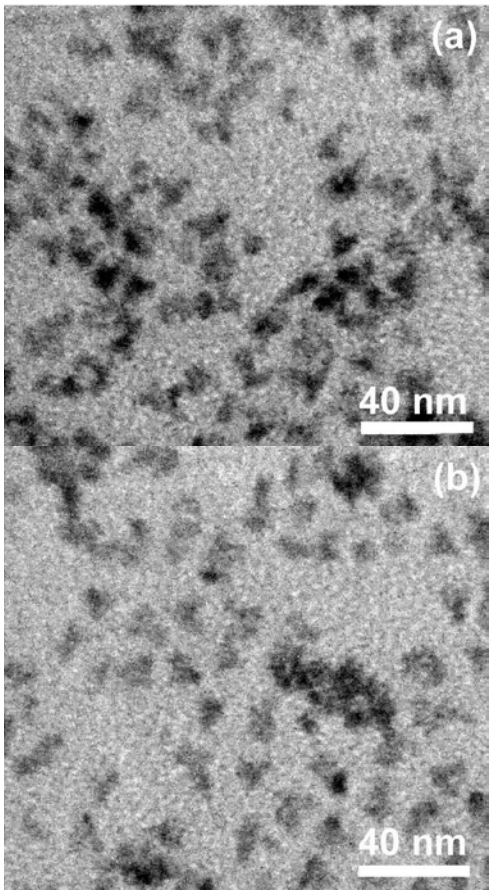

Fig. 3. TEM images of (a) L- and (b) D-cyst-CdS-QDs.

indicating the formation of covalent bonds between sulfur group of cysteine and the surface of CdS-QDs [9]. These observations confirm the successful surface chemical functionalization of CdS-QDs with L- and D- cysteine species.

Fig. 6 shows the UV-Vis absorption and the fluorescence spectra of L- and D-cyst-CdS-QDs. It can be seen that the L- and D-cyst-CdS-QDs show broad absorption edges located at about 440 nm. Their fluorescence spectra show a strong emission at 530 nm and two lower intensity emissions at 457 and 487 nm [23,24].

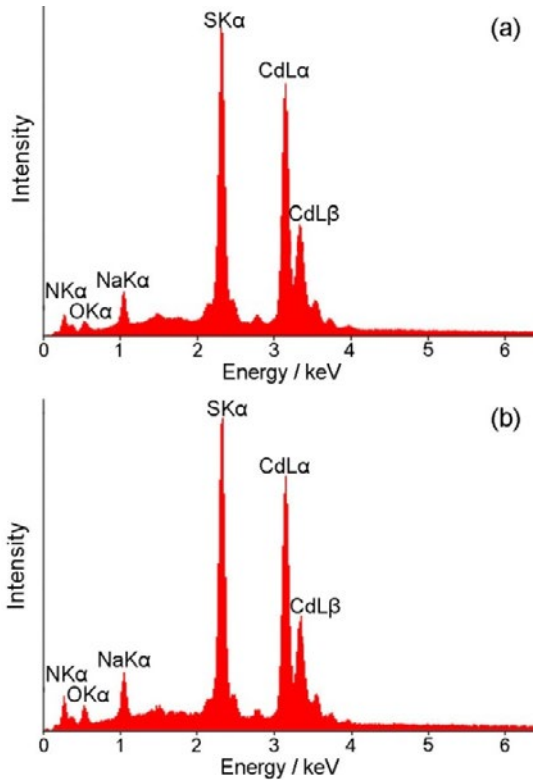

Fig. 4. EDX spectra of (a) L- and (b) D-cyst-CdS-QDs.

Fluorescence studies of the L- and D-cyst-CdS-QDs in the presence of morphine and methamphetamine

Fig. 7 shows the fluorescence spectra of L-cyst-CdS-QDs after addition of various concentrations of L-morphine and D-methamphetamine. As can be seen, the fluorescence intensity of L-cyst-CdS-QDs is decreased with increasing the L-morphine and D-methamphetamine concentrations. Also, the fluorescence spectra of D-cyst-CdS-QDs after addition of various concentrations of L-morphine and D-methamphetamine are shown in Fig. 8. Again, the fluorescence of D-cyst-CdS-QDs is quenched by the addition of L-morphine and D-methamphetamine concentrations.

The mechanism of quenching can be described using the Stern-Volmer equation as follows:

$$\frac{F_0}{F} = 1 + k_{sv}[M]$$

Where F_0 and F are the fluorescence intensities in the absence and presence of quencher (M), respectively. K_{SV} is the Stern-Volmer quenching constant and [M] is the concentration of L-morphine or D-methamphetamine. As shown in the Fig. 9, the obtained Stern-Volmer plots shows good linear relationship between F_0/F and [M] in a low concentration range of L-morphine and D-methamphetamine. According to the Stern-Volmer equation, the linearity of the plots of F_0/F versus [M] indicates the dynamic quenching mechanism.

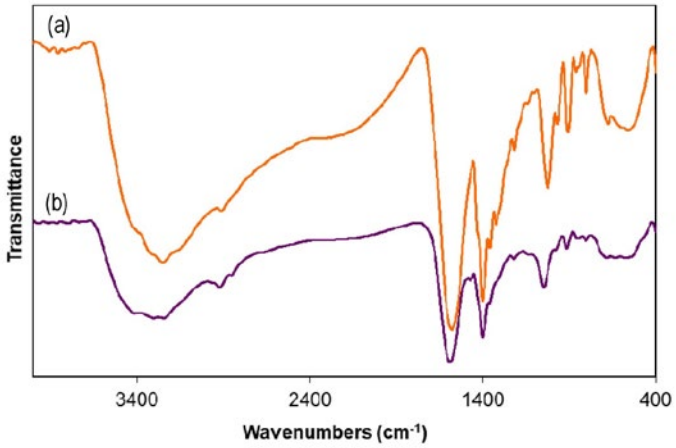

Fig. 5. FT-IR spectra of (a) L- and (b) D-cyst-CdS-QDs.

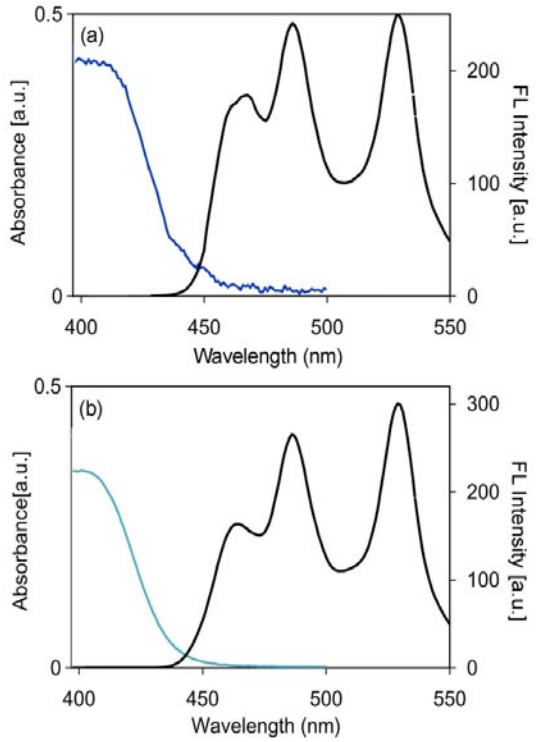

Fig. 6. UV-Vis and fluorescence spectra of (a) L- and (b) D-cyst-CdS-QDs. Excitation wavelength for all fluorescence spectra is 388 nm.

More inspection of the fluorescence quenching of both L- and D-cyst-CdS-QDs in the presence of L-morphine and D-methamphetamine indicated that L-cyst-CdS-QDs has a better interaction with D-methamphetamine rather than L-morphine while D-cyst-CdS-QDs shows reverse trend. The difference in the behavior of the L- and D-cyst-CdS-QDs can be attributed to the existence of chiral L- and D-cysteine species in their structures and different interactions of these chiral species with chiral molecules such as L-morphine and D-methamphetamine. Thus, the enantioselective interaction of the functionalized CdS-QDs with L-morphine and D-methamphetamine resulted in their chiral recognition.

CONCLUSIONS

Water-soluble chiral L- and D-cyst-CdS-QDs were prepared in aqueous solutions at room temperature through a straightforward one-pot process. The applicability of the prepared water-soluble L- and D-cyst-CdS-QDs as fluorescence probes for detection and determination of L-morphine and D-methamphetamine in aqueous solutions was described based on the enantioselective fluorescence quenching of L- and

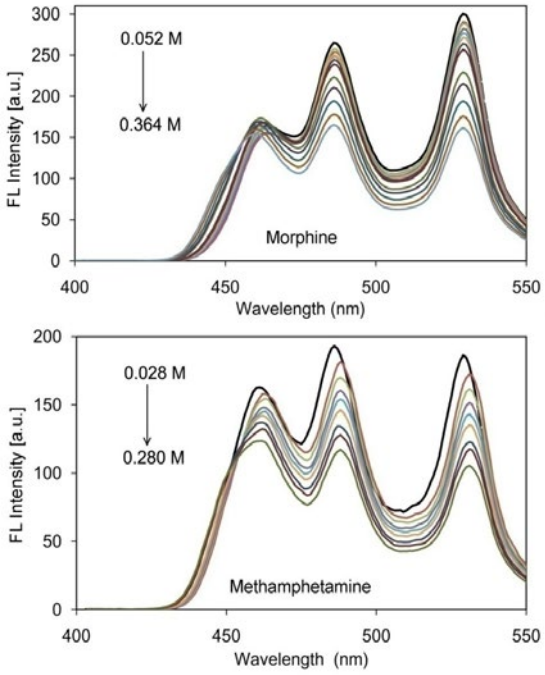

Fig. 7. The fluorescence spectra of L-cyst-CdS-QDs upon addition of the various concentrations of L-morphine and D-methamphetamine.

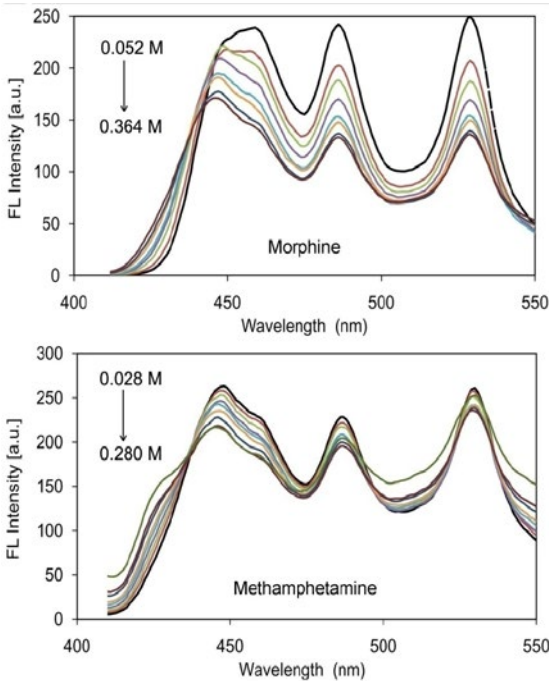

Fig. 8. The fluorescence spectra change of D-cyst-CdS-QDs upon addition of the various concentrations of L-morphine and D-methamphetamine

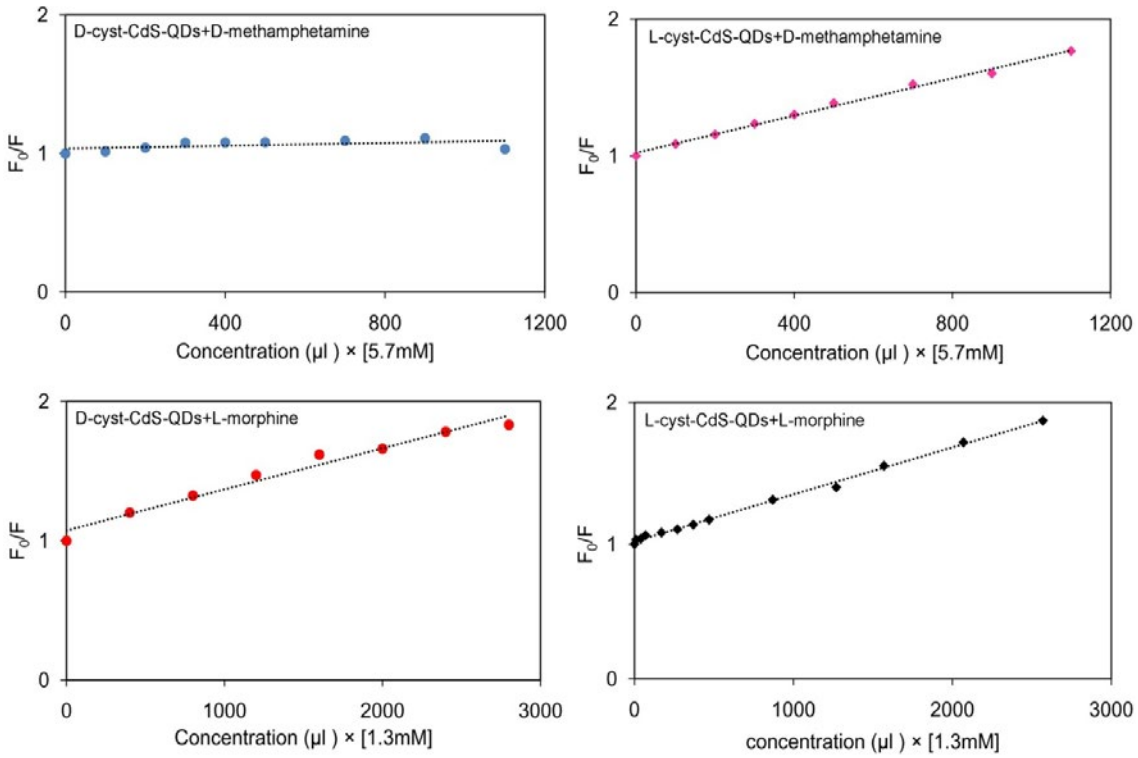

Fig. 9. Stern-Volmer plots of interaction between L- and D-cyst-CdS-QDs and L-morphine and D-methamphetamine.

D-cyst-CdS-QDs in the presence of L-morphine and D-methamphetamine. Compared with organic fluorophores, L- and D-cyst-CdS-QDs as fluorescence probes offer some advantages such as high sensitivity, simple preparation methods, tunable excitation spectra, and good photochemical stability.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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