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Novel aspartic chiral optical sensor based on β-cyclodextrin-functionalized CdTe nanoparticles

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ABSTRACT

Based on the quenching effect of fluorescence intensity of CdTe nanoparticles coated β-cyclodextrin, a novel aspartic chiral assay is suggested. The CdTe nanoparticles were synthesized by co-precipitate and then modified with β-cyclodextrin through a sonication technique to get CdTe@βCD nanoparticles. To characterize CdTe@βCD, FT-IR spectra, fluorescence spectroscopy, and transmission electron microscope were applied. The coupling of host–guest interaction of β-cyclodextrin and aspartic and the fluorescence quenching effect resulted in high selectivity on aspartic of CdTe@βCD sensor. The quenching process was described by the Stern–Volmer equation. The available mechanism of the assay is proposed. Under optimal conditions, the limit of detection of the assay for D-aspartic form was calculated to be 19 ng/mL. The proposed aspartic chiral assay exhibited as a simple and rapid sensing method.

1. Introduction

Semiconductor nanoparticles (NPs) are taken great research interest owing to their size-dependent properties, which are largely attributed to quantum confinement or surface effect. Their unique features include size-dependent optical absorption spectra, large extinction coefficients, and extended photostability [1,2]. Thus, the controlled synthesis of the nanoparticles with defined size and morphology would generate significant opportunities for applications. The main requirement for the analytical use of NPs is capable of binding or occupancy. For this reason, the NPs need to be functionalized by functional groups. One of the important factors to consider functionalized NPs is the maintenance of the original physical properties of the NPs. There are many introductions of organic ligands on the surface of NPs that allow not only the stability of these NPs in different solvents but also the desired surface functionality [3-5]. Among the NPs, CdTe is widely investigated because of its potential use in sensing, optical emission [6-10].

Cyclodextrin (CD), as a well-known molecular host, has been used as an ideal functional molecule to modify the surface of NPs or combine to another material for different purposes, such as chiroselective analysis, cell labeling, cell imaging, drug storage-delivering [11-15], pollutant treatment [16,17], photovoltaic [18], and fluorescent gas probe [19-21]. Cyclodextrin is cyclic (α-1,4)-linked oligosaccharide of α-*gluco*-pyranose containing a relatively hydrophobic central cavity and hydrophilic outer surface. Cyclodextrin has a cone sharp, where the primary hydroxyl groups are located on the narrow side of the cone while secondary hydroxyl groups are located on the wider edge. These confirmations of cyclodextrin result in external hydrophilicity and internal hydrophobicity [22]. There are three types of cyclodextrin, α- to β- to γ-cyclodextrin, which consist of six, seven, and eight glucopyranose units, respectively. Cyclodextrin possesses a distinct possibility of double selectivity because of dependent on the size of the cavity/guest molecule and functional group. The β-cyclodextrin (βCD)-functional optical NPs have been applied to their biocompatibility, chiral selectivity in the biomedical field [12,14,23-25]. Freeman et al. [12] used CdSe/ZnS NP coated with βCD to determine D, L-phenylalanine and D, L-tyrosine based on fluorescence resonance energy transfer (FRET) between NP and Rhodamine. Other reports, βCD capped Ag, TiO_2, and CdTe NPs have been used as a modified NP to develop fluorescent sensors in water media [22,23]. Algarra et al. [23] prepared CdTe NP using

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removed with centrifugation at 5000 rpm for 15 min. The precipitate was re-dispersed in water and re-precipitated by isopropanol. Purification of the CdTe NPs was carried out by repeating the dispersion- precipitation- centrifugation cycle. The prepared CdTe NPs were dried in a vacuum oven at 50 °C for 12 h.

2.4 mg CdTe NPs were dispersed in 5 mL distilled water. A certain amount of βCD was added into the CdTe solution under stirring. The mixture was sonicated by 200 W of power at 40 °C for 10 h to form CdTe@βCD NPs. The product was precipitated with isopropanol, and the CdTe@βCD particles were separated from the solution by centrifugation at 5000 rpm, washed repetitively with isopropanol/ water to remove excess reagents. CdTe@βCD powder was dried at 50 °C in a vacuum oven for 12 hrs.

3. Results & discussion

3.1. FT-IR spectra and morphology of βCD- functionalized CdTe NPs

FT-IR spectra of CdTe NPs before and after coating βCD confirmed the successful binding of βCD and the surface of CdTe, as shown in Fig. 1. The band at 1160 cm^{-1} corresponds to the asymmetric glycosidic vibration νa(C—O—C), the band at 1080 and 1030 cm^{-1} corresponds to the coupled stretch vibration ν(C—C/C—O), and the broad-band at 3400 cm^{-1} arises from the O—H vibration. The appearance of this IR band and those in the fingerprint regions indicate clearly that βCD cannot be removed from the CdTe by extensive washing with deionized water [11]. The absorption band at 1630 cm^{-1} due to carbonyl stretching C=O, which shifted from 1650 cm^{-1} indicated that it was chemisorbed on the surface of CdTe NPs. Also, new bands were detected in the 2700–1850 cm^{-1} range, whereas the FT-IR spectrum of raw βCD only has the stretching $\nu a(CH_2)$ at 2919 cm^{-1} and stretching $\nu s(CH_2)$ at 2849 cm^{-1} [21]. The analysis of the FT-IR spectra has confirmed the incorporation of βCD to CdTe. The intensity of IR peaks increased with the increasing βCD concentration. To ensure the faultless modification of the CdTe surface, the CdTe NPs were modified with an excessive amount of βCD.

The cover of βCD on the surface of CdTe resulted in a decrease in the FL intensity of CdTe@βCD NPs. The FL intensity of CdTe@ βCD NPs was decreased with increasing βCD concentration and got saturation state from the concentration of 20 mmol.L^{-1} βCD, as shown in Fig. 2a. This value was chosen for further study. A distinct difference of absorption spectra of CdTe NP and CdTe@βCD NPs is not found except their intensity (Fig. 2b). It suggested that the coating process did not change the original optical property of original CdTe NPs.

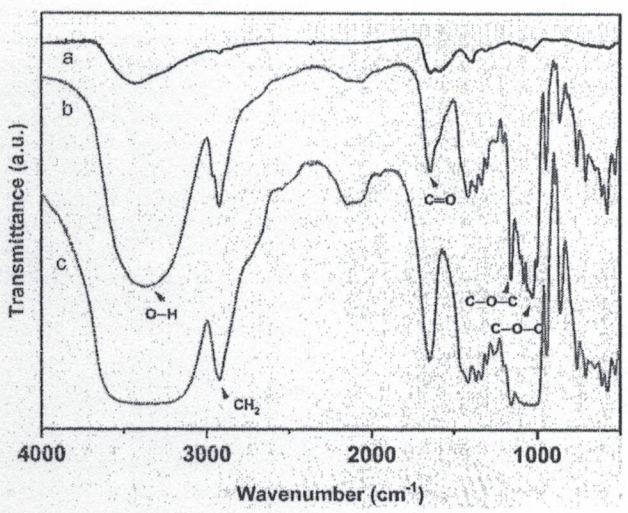

Fig. 1. FT-IR spectra of (a) CdTe, (b) CdTe@βCD NPs, and (c) raw βCD.

The morphologies of the synthesized CdTe and CdTe@ βCD NPs were observed by TEM. As seen in Fig. 3, the TEM images exhibit the near sphere of CdTe@βCD NPs, and the diameter of the CdTe NPs after coating with βCD was increased. A histogram of the particle size distribution (200 samples) is shown at the inset of Fig. 3a and b. The average diameters of nanoparticles were estimated to be 6 nm for the CdTe and 7 nm for CdTe@βCD with a narrow size distribution. The size of CdTe particles was a little smaller than that of CdTe@βCD particles to indicate that βCD was coated on the CdTe NPs. The increase in particle size by TEM and the result of FT-IR spectra confirmed the existence of βCD on the surface of CdTe NPs.

3.2. Photostability of β-CD-functionalized CdTe

The stability of CdTe@βCD NPs in water was estimated by measurement of the FL intensity as a function of time at room temperature. The results showed that CdTe@βCD NPs were stable for 2 weeks, and then the FL intensity was decreased over the following days. But CdTe@βCD NPs powder revealed optical and physical stabilities for months in a dark box. In the process of preparing CdTe@βCD NPs, cyclodextrin molecules were attached to the surface of CdTe NPs. Thus, the surface defect of CdTe NPs could be ulterior passivated, which results in CdTe@βCD NPs becoming more stable. The effect of pH value of the CdTe@βCD solution in the range of 3 – 12 on the FL intensity was investigated using phosphate buffers saline and it was found that the FL intensity of the CdTe@βCD solution was considered stable in the interval 7.0–9.0. The FL intensity of the CdTe@βCD solution was decreased when the pH values of the CdTe@βCD solution were lower than 7 and higher than 9. The result could be originated from the break of the binding of CdTe and βCD, resulting from the appearance of the defects on the surface of CdTe@βCD NPs. Qu's group also reported that the FL intensity of CdTe was decreased quickly at a high pH value, because the base can nucleophilic attack the surface, displacing the surface thiol-ligand and creating surface defects [26]. Therefore, the next chiral recognition experiments were carried out at pH 7.1.

3.3. Chiroselectivity of β-CD-modified CdTe

To investigate the response of FL of CdTe@ βCD to amino acids, the effect of amino acids on FL intensity was performed. The FL intensity of CdTe@ βCD NPs showed a selective quenching effect by aspartic acid over other amino acids. Fig. 4 displays FL response of CdTe@βCD NPs to 10^{-4} M acebutolol, labetalol, ibuprofen, ketoprofen, cetirizine, tryptophan, histidine, and aspartic. It was shown that aspartic, ibuprofen, and ketoprofen can quench the luminescence of CdTe@βCD NPs; but other chiral had very little effect on βCD-modified CdTe NPs. The difference could be due to the size variation from the size cavity of βCD. The quenching luminescence of CdTe@βCD NPs is attributed to the fact that aspartic molecules can enter the cavity of the βCD.

The effect of L-Asp, D-Asp, and DL-aspartic acid on FL intensity is shown in Fig. 5. It was found that the FL intensity of CdTe@βCD NPs was strongly decreased in the presence of D-aspartic acid. In comparison with L-aspartic, the FL intensity of CdTe@βCD NPs was reduced more than 10 times with the addition of D-aspartic. L-aspartic has very little effect on the fluorescent intensity of the CdTe@βCD NPs, indicating that this enantiomer does not associate with the βCD sites. This result allows the impressive chiroselective analysis by the CdTe@ βCD NPs system. The FL intensity of CdTe@βCD NPs was not different when the analytes were ketoprofen, ibuprofen chiral. Thus, CdTe@ βCD NPs can be used for analyzing the chiral compound of aspartic acid. Fig. 6 shows the relationship between FL intensity and the molar ratios of D-aspartic and L-aspartic forms. The results show D-aspartic form strongly affected FL intensity. It means that the CdTe@βCD NPs have high chiroselective properties on aspartic acid.

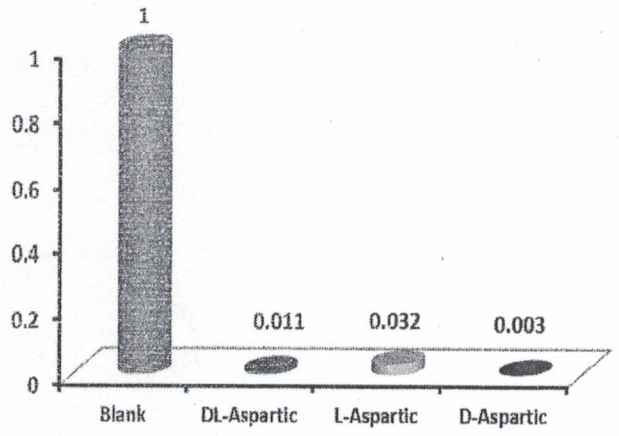

Fig. 5. Effect of D and L form of Asp on FL intensity.

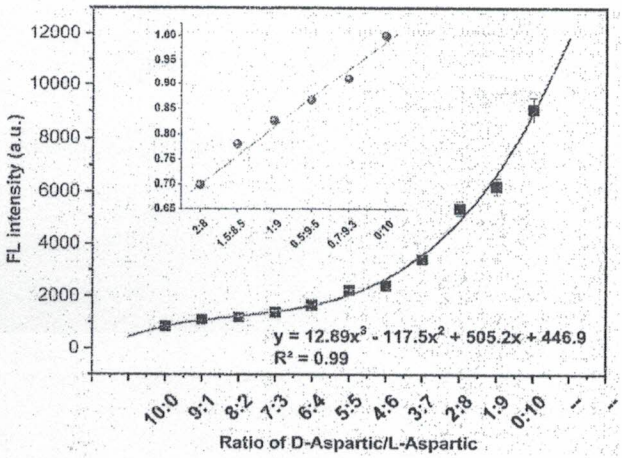

Fig. 6. The relationship between FL intensity and D/L- aspartic form ratio; the inset shows the expansion of range 2:8–0:10 of D/L ratios.

$$\frac{Io}{I} = 1 + K_{SV}[S]$$

where I and I_0 are the fluorescence intensities of the β-CD-modified CdTe NPs at a given related concentration of chiral and in a chiral-free solution, respectively, and [S] is the concentration of chiral. The dependence of I_0/I as a function of [S] is shown in Fig. 7. The K_{SV} term is 65027 M^{-1}. The limit of detection (LOD) calculated according to the 3σ IUPAC criteria, was 19 ng/mL.

The LOD in comparison between this method and other methods is presented in Table 1. LOD of this method has the same order as ion-exchange chromatography and CE method, but it was used at a simple, reasonable price and showed high performance. The quenching luminescence of the βCD-modified CdTe NPs may be attributed to the fact that the aspartic molecules could enter the cavity of the βCD and/or βCD, and then build a complex with aspartic easily through hydrogen bond and/or host–guest interaction. These reasons could cause fluorescence intensity quenching. Since aspartic have no absorption peak in the range of 300 – 700 nm, so we suppose that supra-molecular complexes βCD/aspartic may result in a generation of a new and efficient non-radiative path and/or in the suppression of a radiative process. Therefore, the CdTe@βCD can be used as direct luminescence sensors for aspartic acid that binds to the receptor cavity, and it acts as a trap center on the surface of CdTe@ βCD.

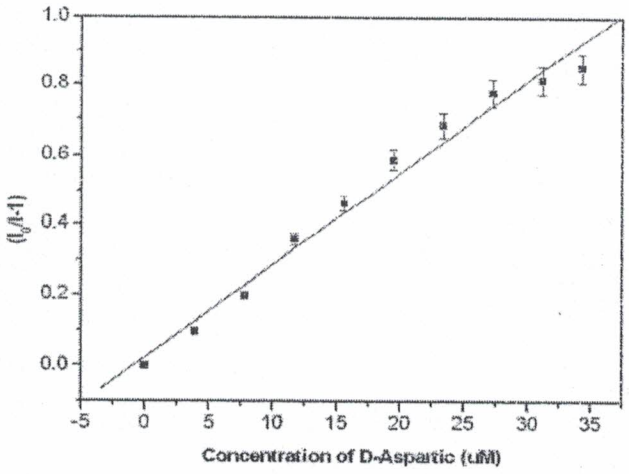

Fig. 7. The relationship between FL intensity and D-aspartic concentration.

Table 1
LOD comparison with other methods.

Method	LOD (ng/mL)	Ref.
CE	8	[26]
Ion exchange chromatography	3	[25]
Copper nanoparticle modified carbon paste electrode	3993	[29]
Molecularly imprinted polymer- electrochemical	2	[30]
CdTe@βCD sensor	19	This work

4. Conclusions

We have developed a simple, low cost and convenient method for the preparation of βCD-modified CdTe as a versatile and chiroselective sensing platform using a fluorescent quenching. The CdTe nanoparticles were functionalized directly by βCD using a modified sonochemical technique. The CdTe@βCD NPs revealed optical and physical stabilities after several months in a dark box. The CdTe@βCD NPs indicated a chiroselective property on aspartic acid. The fluorescent intensity of CdTe@βCD was decreased correspondingly to increasing aspartic concentration in the range of 3 – 31 μM with the calculated LOD of 19 ng/mL. Further study will be investigated to determine the presence of aspartic in real samples.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Declaration of Competing Interest: The authors declare no conflict of interest.

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