



Synthesis of dual-emitting (Gd,Eu)₂O₃-PEI@CD composite and its potential as ratiometric fluorescent sensor for curcumin

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ABSTRACT

Carbon dots (CD)-coated (Gd,Eu)₂O₃-PEI nanospheres were successfully prepared via a facile electrostatic absorption method. Under UV irradiation, the composite simultaneously exhibits both blue CD emission band and red Eu³⁺ emission peaks. It is found that blue CD emission could be quenched by curcumin, while red Eu³⁺ emission is hardly influenced. Thus, a novel self-referencing fluorescent sensor for curcumin with high sensitivity and superior signal discriminability was designed. The ratio of two emissions (F_{445}/F_{611}) shows good linear relationship with curcumin concentration ($R^2 = 0.9973$). The limit of detection is determined to be 0.0615 μg/ml at the signal to noise ratio of 3. These attractive merits enable this composite in ratiometric sensing for medicines in the future.

1. Introduction

Carbon dots (CD) have received great attention in the field of fluorescent nanomaterials owing to their excellent properties such as unique optical properties [1], aqueous solubility [2], photo-stability [3] and low toxic [4]. So the carbon dots have extensive applications in bioimaging [5], heavy metal detection [6], catalysis [7], and drug-loading [8]. Carbon dots for sensing application were widely studied in recent years [9], i.e. the carbon dot-functionalized aerogels could be used for NO₂ sensing [10], and carbon dot-MnO₂ composites were utilized for glutathione detection [11]. It has been found that the carbon dots could be applied in detection of multiple heavy metal ions such as Cu²⁺ [12], Hg²⁺, Pb²⁺, and Cd²⁺ [13].

As an effective constituent of traditional Chinese medicine, curcumin, which is of orange yellow color and bitter taste, has advantages of lipid-lowering, anti-inflammatory, choleresis, anti-tumor and oxidation resistance. Currently, multitudinous investigations have been examined to search the sensitive-methods for curcumin detection, such as high-performance liquid chromatography (HPLC), capillary zone electrophoresis, electrochemical method, and resonance light-scattering [14–17] etc. However, most of the above methods realize their excellent performances at the expense of high cost, time-consuming, complicate sample preparation and sophisticated instruments. As an alternative, fluorescence analysis has become a research hot-spot due to their outstanding properties of high sensitivity and selectivity, facile

operation, wide range and low consumption.

In this work, (Gd,Eu)₂O₃-PEI@CD composites for colorimetric and ratiometric sensing was designed and synthesized by a facile electrostatic absorption method. This composite exhibits dual-emission under single UV excitation by combining rare-earth compounds ((Gd,Eu)₂O₃, red emission) with amino-modified CD (blue emission). It can be used as a ratiometric optical sensor for curcumin since their fluorescence intensity ratio is highly sensitive to the concentration of curcumin due to inner filter and static quenching process. The possibility of detecting the content of curcumin was confirmed by Stern-Volmer equation. It is found that excellent linear relationship between the fluorescence intensity ratio of this composite and the concentration of curcumin was established in the range of 0.2 μg/ml to 3.0 μg/ml. Limit-of-detection as low as 0.0615 μg/ml (3 s) was achieved.

2. Experimental

2.1. Material

Gadolinium(III) nitrate hexahydrate, Europium(III) nitrate hexahydrate, urea, ethylene imine polymer (PEI), ethylenediamine, citric acid, curcumin. All reagents were analytical and the water used in the experiments was deionized water.

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2.2. Synthesis of blue carbon dots (CD)

The blue carbon dots were prepared by hydrothermal method using citric acid and ethylenediamine as raw materials [18]. Briefly, 0.42 g citric acid was dissolved with 10 ml deionized water and then 536 μ l ethylenediamine was injected. The solution was ultrasonicated 10 min, then sealed in a 50 ml Teflon-lined autoclave and heated at 200 °C for 5 h. The obtained dark brownish solution was dialysed by a dialysis bag (Mw = 1000) for 12 h and stored at below 4 °C for further uses.

2.3. Preparation of (Gd,Eu)₂O₃ sphere

By referring the previously reported method [19], the synthesis of (Gd,Eu)₂O₃ sphere was as follow. 7.5 g urea was dissolved with deionized water, into which 4.875 ml Gd(NO₃)₃ (1 M) solution and 0.125 ml Eu(NO₃)₃ (1 M) solution were added. The total capacity was 250 ml. The solution was stirred half an hour at room temperature and then was heated at 90 °C for 2 h. The white precipitate was obtained by centrifuging. After calcining (750°C, 2 h), the final product could be collected as white powder.

2.4. Synthesis of (Gd,Eu)₂O₃-PEI@CD composites

A certain amount of (Gd,Eu)₂O₃ powders were dispersed in 10 ml (5 wt%) solution of PEI and then were stirred 24 h at the room temperature. After centrifuging, the supernatant was discarded and the solid was obtained. The prepared CD (30 ml) was continually added in above solid which stirred for 24 h again. Under the same operation of centrifugation, (Gd,Eu)₂O₃-PEI@CD was synthesized and dried at 80 °C for further application.

2.5. Fluorescent sensing for curcumin

2 ml (Gd,Eu)₂O₃-PEI@CD solution (1 mg/ml) was placed in the cuvette and then 1 ml different concentration of curcumin ranging from 0.2 μ g/ml to 5 μ g/ml was injected in rapidly. The solution was mixed and measured at 310 nm excitation wavelength. The quenching experiment of CD used a similar procedure that using CD instead of (Gd,Eu)₂O₃-PEI@CD. The description of the quenching process utilized the Stern–Volmer equation: $F_0/F_1 = 1 + K_{sv}[C]$, where F_0 and F_1 represent the fluorescence peak strength of (Gd,Eu)₂O₃-PEI@CD in the absence and existence of curcumin, respectively, and $[C]$ is the concentration of curcumin.

2.6. Characterization

The solids for X-ray diffraction (XRD) patterns were obtained using RINT 2200 Science diffractometer. The field emission scanning electron microscopy (JSM-7001 F) was used to observe the morphology and size of all samples. The FT-IR spectrum of (Gd,Eu)₂O₃-PEI@CD was recorded in the range of 400–4000 cm^{-1} with PerKin Elmer FT-IR spectrometer Frontier using samples embedded in KBr tablet. UV–vis absorption spectra of samples were collected on UV-3600 (Shimadzu, Japan). Fluorescence spectra and lifetime decay curves of samples were measured with FLS980 fluorescence spectrometer (Edinburgh, UK). The zeta potential values of samples were obtained on a Nano ZS zeta potential analyzer (Malvern, UK).

3. Results and discussion

3.1. Structure and morphology studies of (Gd,Eu)₂O₃-PEI@CD

Fluorescence of (Gd,Eu)₂O₃-PEI@CD and their sensing for curcumin were illustrated in Scheme 1. Firstly, ethylene imine polymer (PEI), a positive charge polymer, was used to functionalize the (Gd,Eu)₂O₃ spheres, which results in the sample possessing positive charge. It can

offer attractive forces for negative-charged substance such as carbon dots. The prepared (Gd,Eu)₂O₃-PEI@CD is able to emit the blue fluorescence (445 nm) and red fluorescence (611 nm). When curcumin is introduced, the peak intensity of blue-emission decrease evidently, meanwhile, the red-emission remains unchanged. Furthermore, the ratio of dual-emission (F_{445}/F_{611}) has good linear relation ($R^2 = 0.9973$) with curcumin concentration. Thus, (Gd,Eu)₂O₃-PEI@CD could be used as a ratiometric fluorescent sensor for curcumin.

XRD was used to check the phase purity of all samples. Fig. 1 gives the XRD pattern and SEM image of samples. It is clearly that the diffraction peaks of three samples were fairly matched with the Gd₂O₃ phase (JCPDS 88–2165), indicating that modified with PEI and absorbed with CD dot not change phase structure of Gd₂O₃ because PEI or CD absorbed in Gd₂O₃ is amorphous. Additionally, the SEM image affirms that morphology of Gd₂O₃ is spherical with average diameter about 250 nm with smooth surface. The (Gd,Eu)₂O₃-PEI@CD also displays glossy sphere and same size with no significant variation comparing with Gd₂O₃. The consequence illustrates that decoration with PEI or CD causes no obvious change on morphology and size of Gd₂O₃. From UV–vis spectra (Fig. 2a), it can be observed that a strong absorption peak of (Gd,Eu)₂O₃ and (Gd,Eu)₂O₃-PEI@CD both appear at about 275 nm due to the energy transfer from Gd³⁺ to Eu³⁺, assigning to the ⁸S_{7/2}–⁶I_J transition of Gd³⁺. The absorption band at 220 nm is due to the 4f–5d transition of Gd³⁺. Band gap energy of bulk Gd₂O₃ is 5.40 eV (230 nm) and that of nano-Gd₂O₃ is 5.60 eV (220 nm) [20]. This result suggests a blue shift which can be attributed to the quantum confinement due to small size of Gd₂O₃ nano-particles. (Gd,Eu)₂O₃-PEI@CD has another broad absorption peak at 360 nm, which can be attributed to the n- π^* transition from –CONH– bond of blue carbon dots. These features are consistent with the following excitation spectra of the samples. As shown in Fig. 2b, the all samples exhibit similar FT-IR spectra, thus explaining the presence of some alike chemical functional groups. Several characteristic peaks appear at about 3141 cm^{-1} , 1686 cm^{-1} , 1400 cm^{-1} , 1041 cm^{-1} and 547 cm^{-1} . The peak at 3141 cm^{-1} can be attributed to O–H stretching vibration, and those at 1686 cm^{-1} and 1041 cm^{-1} are ascribed to C=O and C–N stretching vibration, respectively. The peak at 547 cm^{-1} can be assigned to the Gd–O stretching frequencies of Gd₂O₃ [21]. The result is consistent with that of XRD pattern and confirms the formation of crystalline Gd₂O₃ nanocomposites. These results mean that the surface of (Gd,Eu)₂O₃-PEI@CD are rich in hydrophilic group including hydroxyl group, carboxyl group, and amide group, which confirmed that the CD have been successfully attached with the surface of (Gd,Eu)₂O₃. The apparent zeta potential graph can be seen in Fig. 3. The zeta potential of CD and (Gd,Eu)₂O₃-PEI are -5.08 mV and + 22.0 mV, respectively, which is reduced to + 19.5 mV in (Gd,Eu)₂O₃-PEI@CD by electrostatic effect.

3.2. Fluorescent characteristic of samples

To understand the fluorescent characteristics of samples, the PL and PLE spectra were measured. Fig. 4 shows the excitation and emission spectra of CD and (Gd,Eu)₂O₃-PEI@CD composites. As shown in Fig. 4a, CD exhibits an intense absorption band at 360 nm in range of 300–420 nm. When excited at optimal wavelength (360 nm), the CD solution shows an intense blue emission band with peak wavelength at 445 nm. Meanwhile, the curcumin has no luminescence at 360 nm UV excitation. Fig. 4a also shows that strong absorption peak of curcumin appears at 430 nm. From Fig. 4b, (Gd,Eu)₂O₃-PEI@CD simultaneously shows the dual-emission peaks at 445 nm and 611 nm upon single 310 nm excitation. The PL spectrum consists of a broad blue-emission band from carbon dots and the narrow red-emission peaks of Eu³⁺. Thus, the recombination of electron-hole pairs in the strongly localized π and π^* electronic levels of the sp² sites is responsible for the appearance of broad emission band at 445 nm. The sharp emission peaks ranging from 550 nm to 700 nm are assigned to the transition from ⁵D₀ to ⁷F_J (J = 0, 1, 2, 3, 4) of Eu³⁺. The dominant emission peak centered

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