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The development of a new optical sensor based on the Mn doped ZnS quantum dots modified with the molecularly imprinted polymers for sensitive recognition of florfenicol

Susan Sadeghi *, Moslem Jahani, Foroogh Belador

Department of Chemistry, Faculty of Science, University of Birjand, Birjand, Iran

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ABSTRACT

The Mn doped ZnS quantum dots (Mn:ZnS QDs) capped with the florfenicol molecularly imprinted polymer (Mn:ZnS QDs@MIP) were prepared via the sol–gel surface imprinting approach using 3-aminopropyltriethoxysilane (APTES) as the functional monomer and tetraethoxysilane (TEOS) as the cross-linker for the optosensing of the florfenicol. Transmission electron microscopy (TEM), X-ray diffractometer, IR spectroscopy, UV–Vis absorption spectrophotometry, and spectrofluorometry were used to elucidate the formation, morphology, and identification of the products. To illustrate the usefulness of the new imprinted material, the non-imprinted coated Mn:ZnS QDs (Mn:ZnS QDs@NIP) were synthesized without the presence of the florfenicol. It was revealed that the fluorescence (FL) intensity of the Mn:ZnS QDs@MIP increased with increasing the FF concentration. Under the optimal conditions, changes in the FL intensity in the presence of the target molecule showed a linear response in the concentration range of 30–700 μmol L^{-1} with a detection limit of 24 μmol L^{-1}. The developed method was finally applied successfully to the determination of FF in different meat samples with satisfactory recoveries.

1. Introduction

Quantum dots are attractive nano-particles made of semiconductor materials from groups II and VI or groups III and V of elements with high luminescence property such as CdSe, CdS, CdTe, and ZnS [1,2]. They show unique optical and electronic properties, such as sharp emission band with broad excitation wavelengths, good photostability and tunable emission peaks that make them superior to conventional organic fluorophores. Many studies in the field of synthesis and applications of QDs in various areas such as bio-diagnostics, bio-imaging, photonics, optoelectronics, and sensors have been reported [3,4]. Their broad absorption spectra with narrow emission spectra make it possible to excite different QDs of different sizes with a single wavelength excitation source. Therefore, QDs are suitable for multiplexed analysis of complex biological systems [5]. Nowadays a few chemo-sensors have been reported for determination of various analytes based on the change in fluorescence intensity of QDs [6–9].

The nano-phosphors and especially sulfides doped with transition metals semiconductors in which the doped ions act as luminescence centers have excellent optical properties that differ from the corresponding host nano-materials [10,11]. Among them, zinc sulfide QDs with less toxicity than other QDs and wide band gap energy as a luminescent host material for various dopants can be used to increase the photoluminescent efficiency of the resulting semi-conductive nano-particles [12,13]. Mn-doped ZnS quantum dot (Mn:ZnS QD) is a non-toxic ZnS semiconductor doped with manganese impurities, and has been used as an ideal fluorescence labeling agent. The ZnS nano-particles present fluorescence signal in the ultraviolet region, while the fluorescence signal of Mn:ZnS QD nano-particles lies in the visible region due to triplet transition of Mn^{2+} ions incorporated into the ZnS host lattice [14]. Due to high quantum yield, biocompatibility, highly active surface areas with an isoelectric point of about 7, the strong orange emission band about 600 nm, and higher fluorescence life of Mn:ZnS QDs than that of conventional QDs such as CdS, CdSe, and CdTe, they have been extensively used as a fluorescent sensor in various applications [7,9,11].

Surface functionalization of the QDs via capping agents such as thioglycolic acid (TGA), mercapto ethanol, thioglycerol, and 3-mercaptopropionic acid, is a promising way to enhance their specific properties such as control the size, increase the stability, prevent the aggregation as well as increase selectivity of nano-particles [15].

The application of the molecularly imprinted polymers (MIPs) as a capping agent can greatly improve the selectivity of the luminescence QDs. In imprinting process, polymerization of functional monomers occurs in the presence of the template molecule for creating the specific

* Corresponding author.
E-mail address: ssadeghi@birjand.ac.ir (S. Sadeghi).

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binding sites within the polymeric structure. Removal of the template molecules leaves binding sites that are complementary in the shape and functionality to the template molecule. The specific properties of MIPs such as good stability, selectivity and re-usability make them more suitable for use in different fields such as separation, diagnostic assays, sensors and catalysts [16,17].

Florfenicol (FF), as a member of the fenicol class of antibiotics especially developed for veterinary medicine, has been used for treatment of bovine respiratory pathogens since 1995. Its structural and antimicrobial properties are similar to chloramphenicol (CAP) and thiamphenicol (TAP), but it is significantly more active than CAP [18,19]. The use of CAP in food-producing animals is prohibited and FF can be used as a suitable alternative [20]. FF is widely used in many countries in control of bacterial infections, but there are some reports on bacterial resistance against to FF [21].

In this study, Mn^{2+}-doped ZnS QDs have been synthesized by the chemical co-precipitation method at room temperature. Then, the Mn:ZnS QDs were modified by the FF surface imprinted polymer through a two step procedure. The imprinted layer was fabricated by the sol–gel method with APTES and TEOS as functional monomers and cross-linker agents, respectively. After removing the template, the prepared composite was used as an optical sensor for the determination of FF. In this report, the fluorescence property of Mn-doped ZnS QDs was employed to establish a method for the rapid, facile, selective, and inexpensive detection of FF. In this situation, the advantages of surface molecular imprinting and fluorescence property of QDs are combined together. To the best of our knowledge, the application of such Mn:ZnS QD based MIP in the determination of FF has not been reported yet.

2. Experimental

2.1. Reagents and materials

FF was kindly donated from Erfan Darou Pharmaceutical Company (Tehran, Iran). Chloramphenicol (CAP) was purchased from Sigma-Aldrich Corporation (Missouri, USA) and used as obtained. Zinc sulfate ($ZnSO_4 \cdot 2H_2O$), manganese chloride ($MnCl_2.4H_2O$), sodium sulfide ($Na_2S.5H_2O$) and thioglycolic acid (TGA) were obtained from Merck (Darmstadt, Germany) and were used in the preparation of the manganese doped zinc sulfide quantum dots. The 3-aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS) were provided from Merck and used as the functional monomer and cross-linker agents respectively, in the synthesis of the imprinted sol–gel layer. Ethanol (EtOH), methanol (MeOH), acetonitrile (MeCN), ammonium hydroxide (NH_4OH), acetic acid (HOAc), n-hexane and other organic solvents were purchased from Merck and used as received without any purification. Doubly deionized water (DDW, 18.0 MΩ cm^{-1}) was obtained from an Aqua Max ultra pure water system (Young Lin, Korea).

2.2. Synthesis of Mn^{2+} doped ZnS QDs (Mn ZnS QDs)

The Mn doped zinc sulfide quantum dots (Mn:ZnS QDs) were synthesized by a simple chemical co-precipitation method according to Liu et al. [22]. Briefly, in a 100 mL three-necked flask, $ZnSO_4 \cdot 2H_2O$ (12.5 mmol) and $MnCl_2 \cdot 4H_2O$ (1 mmol) were dissolved in 40 mL DDW. The mixture was stirred for 10 min under inert atmosphere of N_2 and afterwards, 10 mL solution containing 12.5 mmol of sodium sulfide was added drop wisely. The resultant suspension was stirred for another 30 min. At the next step, 10 mL solution of TGA in ethanol (0.625 mmol) was added to the suspension and the mixture was stirred for 20 h. Finally, the Mn:ZnS QDs were obtained following centrifugation, washing with DDW and absolute ethanol three times, and dried in an oven at 50 °C.

2.3. Preparation of MIP-coated Mn:ZnS QDs (Mn:ZnS QDs@MIP)

The MIP-coated Mn:ZnS QD (Mn:ZnS QDs@MIP) preparation process includes TGA capped Mn:ZnS QD assembly of APTES and formation of recognition sites on the surface of the Mn:ZnS QDs.

In the first step, 0.1 g FF was dissolved in 8 mL of absolute ethanol, mixed with 0.15 mL of APTES (functional monomer) and stirred for 1 h at room temperature. At the next stage, 0.59 mL of TEOS (crossing linker) was added into the resultant mixture and stirred for 5 min. Then, 300 mg of TGA-capped Mn:ZnS QDs and ammonia solution were added to the mixture and was stirred for 16 h. This imprinted material was named Mn:ZnS QDs@MIP. The non-imprinted polymer coated Mn:ZnS QDs (Mn:ZnS QDs@NIP) was synthesized in the same procedure without the addition of FF to evaluate the molecular recognition properties of the imprinted material. The preparation process of Mn:ZnS QDs@MIP is presented schematically in Fig. 1.

2.4. Characterization

The X-ray diffraction (XRD) patterns were collected on a D8 Advanced Bruker X-ray diffractometer (Bruker, Germany) with Cu Kα ($\lambda = 1.5406$ Å) radiation in the scan range $2\theta = 10°–70°$. Infrared spectra of the synthesized Mn:ZnS QDs@MIP and Mn:ZnS QDs@NIP in KBr were recorded (4000–600 cm^{-1}) using a Perkin-Elmer 781 infrared spectrophotometer (Perkin-Elmer Ltd, Buckinghamshire, England). Ultraviolet–visible spectra (200–800 nm) were recorded on a Shimadzu 2501 PC UV–Vis spectrophotometer (Shimadzu, Japan). The shape and size of the Mn:ZnS QDs were examined via transmission electron microscopy (TEM) using a Zeiss EM900 transmission electron microscope (Carl-Zeiss, Germany) operating at 80 keV. The photoluminescence spectra of fluorescence measurements of quantum dots were recorded using a RF-5301PC spectrofluorometer (Shimadzu, Japan) equipped with a xenon discharge lamp and a quartz cuvette (1.0 cm optical path).

2.5. Fluorescence measurements

The fluorescence measurements were used to study the selective binding of FF molecules to the Mn:ZnS QDs coated with the MIP or NIP layer. The fluorescence spectra of the Mn:ZnS QDs@MIP and Mn:ZnS QDs@NIP were recorded at excitation and emission wavelengths of 268 and 588 nm, respectively (or scanning in the wavelength range of 220–770 nm). The slit widths of the excitation and emission were both 5 nm. In all experiments, constant weight of the synthesized Mn:ZnS QDs@MIP or Mn:ZnS QDs@NIP was dispersed in a certain volume of the solvent to make a 0.1 g L^{-1} solution and the FL intensities were recorded. The determination of FF was based on the changes in FL intensity, $F–F_0$, where F_0 and F were the fluorescence intensities of the nano-particles before and after addition of the template molecule, respectively. All optical measurements were carried out under ambient temperature (25 °C).

2.6. Analysis of tissue samples

Tissue samples (chicken and fish) were purchased from local markets and were chopped and grounded. Then, 2 g of the tissue was transferred into a 50 mL polyethylene vessel and spiked with florfenicol (at three different levels). After shaking for 30 min, 6 mL of ethylacetate solution (83%, v/v) was added and the resultant mixture was homogenized in an ultrasonic bath (Branson 1510R-MTH ultrasonic bath, BRANSON ultrasonic corporation, Danbury, USA) for 10 min, centrifuged for 5 min in 5000 rpm and the supernatant was transferred to another tube. The extraction step was repeated two times and the supernatants were combined together. The combined supernatant was evaporated to near dryness at 60 °C and the residue was dissolved in 10 mL of DDW. After addition of 5 mL n-hexane, it was vigorously mixed and centrifuged at 6000 rpm for 10 min, and the hexane layer