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A novel dual-function molecularly imprinted polymer on CdTe/ZnS quantum dots for highly selective and sensitive determination of ractopamine

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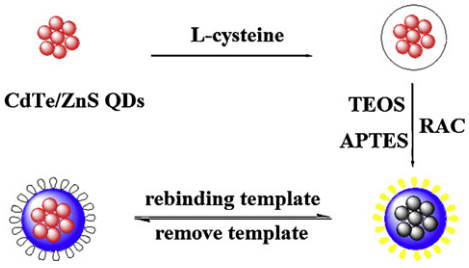
HIGHLIGHTS

- We have developed a novel dual-function MIP-coated QDs material.
- The MIP-coated QDs combine the advantage of molecular imprinting and QDs.
- We used MIP-coated QDs as fluorescence sensing material for recognize RAC.
- We used QDs@MIP as sorbent to combine SPE with HPLC for the determination.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel dual-function material was synthesized by anchoring a molecularly imprinted polymer (MIP) layer on CdTe/ZnS quantum dots (QDs) using a sol–gel with surface imprinting. The material exhibited highly selective and sensitive determination of ractopamine (RAC) through spectrofluorometry and solid-phase extraction (SPE) coupled with high performance liquid chromatography (HPLC). A series of adsorption experiments revealed that the material showed high selectivity, good adsorption capacity and a fast mass transfer rate. Fluorescence from the MIP-coated QDs was more strongly quenched by RAC than that of the non-imprinted polymer, which indicated that the MIP-coated QDs acted as a fluorescence sensing material could recognize RAC. In addition, the MIP-coated QDs as a sorbent was also shown to be promising for SPE coupled with HPLC for the determination of trace RAC in feeding stuffs and pork samples. Under optimal conditions, the spectrofluorometry and SPE-HPLC methods using the MIP-coated QDs had linear ranges of 5.00×10^{-10}–3.55×10^{-7} and 1.50×10^{-10}–8.90×10^{-8} mol L^{-1}, respectively, with limits of detection of 1.47×10^{-10} and 8.30×10^{-11} mol L^{-1}, the relative standard deviations for six repeat experiments of RAC (2.90×10^{-9} mol L^{-1}) were below 2.83% and 7.11%.

1. Introduction

Molecularly imprinted polymers (MIPs) are prepared by synthesizing a network polymer in the presence of a template molecule, after elution of the template, complementary binding sites are revealed within the polymer network that allow rebinding of the template with a high specificity, sometimes comparable to that of antibodies [1]. Surface imprinted sol–gels, in which the imprinted templates are situated at the surface or in close proximity to the surface of a material, possess many advantages such as easier extraction of the original template, smaller particle size, larger surface area, higher binding capacity and faster mass transfer than traditional MIPs.

Quantum dots (QDs) are fluorescent nanomaterials with size-dependent emission wavelengths, high luminescence efficiency and good photostability. QDs also have the ability to form

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complexes with biomolecules [2–4], so the focus on QDs has been growing in recent years. The advantages of highly selective MIPs combined with the high sensitivity of fluorescence (FL) sensing of QDs can be used to reduce the limit of detection (LOD) and analyze trace substances in samples [5–9]. For example, Wang et al. [10] prefabricated MIPs by anchoring an MIP layer on the surface of Mn-doped ZnS QDs *via* a surface molecular imprinting process. Mn-doped ZnS QDs have been used to detect enoxacin in biological fluids [11]. Zhang et al. [12] prepared MIP-coated QDs *via* a sol–gel reaction (imprinting process) for selective recognition of the template cytochrome *c*. Stringer et al. [13] combined MIP microparticles and FL QDs through a simple cross-linking procedure to detect aqueous 2,4-dinitrotoluene. We developed MIP on ionic liquid-modified CdSe/ZnS QDs for the highly selective and sensitive optosensing of tocopherol [14].

To illustrate the usefulness of the new protocol for the MIP-coated QDs material, ractopamine (RAC) was chosen as the target. RAC is a nutrient repartitioning agent, that can promote muscle growth and protein deposition in animals, but it also readily accumulates in animal tissues if used improperly, and may have adverse effects on human health. Therefore, it is important to detect RAC residues in samples. Recently, many analytical methods, high-performance liquid chromatography (HPLC) [15,16], gas chromatography [17], gas chromatography–mass spectrometry [18], liquid chromatography–mass spectrometry [19,20], and ELISA [21–23], MIP extraction coupled with HPLC [24,25] and MIP-electrochemical sensor [26,27] have been developed for detecting RAC residue.

In this study, we proposed novel detection methods using dual-function material of MIP-coated QDs for highly selective and sensitive determination of RAC from feeding stuffs and pork. On the one hand, the MIP-coated QDs act as a sensing material for spectrofluorometric determination of RAC; on the other hand, the MIP-coated QDs behave as a sorbent to combine traditional solid-phase extraction (SPE) with HPLC for enrichment and detection of RAC. Each approach has many advantages, which are described and discussed in detail below.

2. Materials and methods

2.1. Materials

Tellurium powder and RAC were purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd. (Tianjin, China) and Changzhou Huaren Chemical Co., Ltd. (Changzhou, China), respectively. L-Cysteine (BIO Basic Inc, Toronto, Canada), $CdCl_2{\cdot}2.5H_2O$, $ZnCl_2$ (Third Chemical Reagent Factory of Tianjin, China) and Na_2S, $NaBH_4$ (Tianjin Daofu Chemical New Tech Development Co., Ltd., China) were used to prepare CdTe/ZnS QDs. Anhydrous sodium sulfate, NaCl, NaOH, methanol, hexane and acetonitrile were purchased from the Northern Hospital of Tianjin Chemical Reagent Factory (Tianjin, China). 3-Aminopropyltriethoxysilane (APTES) and tetraethoxysilane (TEOS) were procured from Wuhan University Silicone New Material Co., Ltd. (Wuhan, China). Terbutaline (TER), isoxsuprine (ISOX) and isoproterenol (ISOP) were purchased from Sigma–Aldrich (USA). Phosphate-buffered saline (PBS) (10 m mol L^{-1} of PBS pH = 6.8) was used in the experiments. Doubly deionized water (DDW, 18.2 MΩ cm^{-1}) was obtained from a Water Pro water purification system (Labconco, USA).

2.2. Instruments

FL measurements were performed on an F-4500 spectrofluorometer (Hitachi, Japan) equipped with a quartz cell (1 cm × 1 cm). UV–vis spectra (200–800 nm) were recorded on a Cary 50-Bio UV spectrometer (Victoria, Australia). A VisiprepTM-DL SPE vacuum manifold from Supelco (Bellefonte, PA, USA) was used in the preconcentration procedure. Transmission electron microscope (TEM) images were obtained on a 2010 FEF microscope (JEOL, Tokyo, Japan). Samples for TEM analysis were obtained by drying droplets of the sample in absolute alcohol on a 300-mesh Cu grid coated with a lacey carbon film. Fourier transform infrared (FT-IR) spectra (4000–400 cm^{-1}) were recorded using KBr pellets in a Vector 22 FT-IR spectrophotometer (Bruker, Germany). The BET surface area of the QDs was measured on a Quantachrome Autosorb-1, USA.

2.3. Synthesized of water-soluble CdTe/ZnS QDs

Water-soluble CdTe/ZnS QDs were prepared based on the procedure developed by Liu and Yu [28] with minor modification. In a typical experiment, $CdCl_2{\cdot}2.5H_2O$ (0.4 mmol), L-cysteine (0.8 mmol) and distilled water (100 mL) were mixed in a three-necked flask to form the cadmium precursor. The mixture was adjusted to pH 11 with NaOH (1.0 mol L^{-1}), and then stirred under N_2 for 30 min before freshly prepared NaHTe aqueous solution (1.6 mL) containing $NaBH_4$ (0.8 g) and Te powder (0.16 g) were quickly injected into the stirred mixture. The solution was heated at 100 °C for 1 h, cooled to room temperature, and added dropwise to an aqueous solution (50 mL) of $ZnCl_2$ (1 mmol L^{-1}) and Na_2S (1 mmol L^{-1}). The solution heated under reflux at 100 °C, and it began to fluoresce and could be tuned in color by prolonging the heating time. After heating for a certain time, L-cysteine stabilized CdTe/ZnS QDs exhibiting strong fluorescence at 570 nm were obtained. The synthesized CdTe/ZnS QDs were purified by centrifugation and then dissolved in DDW and stored at 4 °C in a refrigerator prior to use.

2.4. Preparation of the sol–gel MIP-coated QDs

RAC template (0.5 g) was dissolved in methanol (3 mL), mixed with APTES (functional monomer, 0.13 mL), and then CdTe/ZnS QDs (4 mL) was added. The mixture was stirred for 50 min before TEOS (cross-linker, 0.126 mL) was added. After stirring for another 30 min, the mixture was sealed and then placed in a water bath at 40 °C for 24 h. After polymerization, the product was purified by centrifugation, and then washed with methanol until no template was detected by UV–vis spectrophotometry. Finally, the MIP-coated QDs were dried in a vacuum oven at 40 °C for 10 h. As a reference, non-imprinted polymer (NIP)-coated QDs were prepared using the same procedure but without addition of the template molecule.

2.5. Binding study

In order to examine the effectiveness of the synthesized material, MIP and NIP-coated QDs nanoparticles (10 mg) were dispersed in a 25 mL round-bottomed flask, containing RAC standard solution (10 mL) of a given concentration in methanol. After shaking for several hours at room temperature, the template had bound to the binding sites, causing FL quenching of the QDs. Adsorption and competitive recognition studies were performed using MIP-coated QDs (10 mg) in methanol solutions of RAC, ISOP, TER, and ISOX (100 mg L^{-1}).

2.6. Fluorescence measurements

All FL detections were performed under the same conditions: the slit widths of excitation and emission were 3 and 5 nm, respectively, and the excitation wavelength was set at 360 nm with a recording emission range of 500–700 nm. MIP- or NIP-coated QDs powder (5 mg, 200 mesh screen), and RAC solution of the desired