



Contents lists available at ScienceDirect

## Sensors and Actuators B: Chemical

journal homepage: [www.elsevier.com/locate/snb](http://www.elsevier.com/locate/snb)



### Research Paper

# Fabrication and evaluation of sulfanilamide-imprinted composite sensors by developing a custom-tailored strategy

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### ARTICLE INFO

#### Article history:

Received 14 March 2017  
Received in revised form 1 September 2017  
Accepted 13 September 2017  
Available online xxx

#### Keywords:

CdTe quantum dots  
Fluorescence detection  
Surface molecular imprinted polymers  
Sulfonamide

### ABSTRACT

In this paper, we have presented a custom-tailored strategy to fabricate molecularly imprinted composite sensors (MIPs/QDs@SiO<sub>2</sub>) with highly selective recognition ability for the determination of sulfanilamides (SAs). The modified SiO<sub>2</sub> sphere, modified QDs, acrylamide (AM), and ethyl glycol dimethacrylate (EGDMA) were used as the supporter, the fluorescent material, the functional monomer, and the cross-linker, respectively. Afterward, a two-step imprinting polymerization reaction was implemented to fabricate the novel sensor MIPs/QDs@SiO<sub>2</sub>. Attributing to the SiO<sub>2</sub> with the surface functional monomer and the QDs with functional group, SAs molecules are attracted to the QDs and bound to the SiO<sub>2</sub> surface, hence accelerating the growth of homogeneous recognition sites on the surface of SiO<sub>2</sub> and guaranteeing the distance between the recognition sites and the QDs. After the experimental conditions were optimized, such fluorescence sensors can be used for well selective detection of SAs with a linear range of 2.0–30 μmol/L and a limit of detection is 0.17 μmol/L. Most importantly, the MIPs/QDs@SiO<sub>2</sub> can be successfully applied to the determination of SAs in real river water, which demonstrate high selectivity and stability and offer a promising platform for detecting environmental pollutants.

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## 1. Introduction

Sulfonamides (SAs) as synthetic antibiotics are used in formulated feed in aquaculture and are also widely designed to prevent the growth of bacteria and treat animal infections from some microorganisms and protozoa due to their possess main advantages including high efficacy, low cost and broad antibacterial spectrum [1,2]. However, sulfonamides and their metabolites are not completely degraded in the environments so that the existence of SAs residues in the food chain have attracted enormous attentions due to their adverse effects to human health, such as the potential carcinogenic nature, the feasible occurrence of antibiotic resistance and allergic reactions in oversensitive persons [1,3,4]. According to the standards to safeguard human health which is established by the European Union (EU), the maximum residue limit of the total amount of SAs in foods from animal origin is 100 μg/kg [5,6]. To date, a variety of analytical methods have been established

for the determination of SAs, such as high-performance liquid chromatography (HPLC) [7], capillary electrophoresis (CE) [8], UV spectrophotometry [9], liquid chromatography tandem mass spectrometry (LC-MS/MS) [10] and so on. However, these methods have deficiencies, including high cost, low selectivity, long analysis time intervals, and tedious sample pretreatment. Therefore, it is necessary to develop new analytical methods for the detection of SAs in the environment.

Quantum dots (QDs) have received considerable attentions due to their unique optical properties including high luminescence efficiency, size-tunable emission wavelengths, narrow symmetric emission and excellent photostability [11–17]. A variety of QDs have been applying for the design of fluorescence sensors and biological probes with different applications in bioanalysis, environmental analysis and clinical or medical detection [18–22]. To improve the selectivity of QDs-based sensors, molecular imprinting as a powerful technique which is for synthesizing three-dimensional cross-linked polymers with specific recognition sites has been frequently used in recent years [23–27]. Its products are created by the copolymerization of functional monomers and cross linkers in the presence of the template molecules, which are named molecularly imprinted polymers (MIPs) [28–30]. How-

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<http://dx.doi.org/10.1016/j.snb.2017.09.081>

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ever, due to the highly cross-linked structure has limited these molecules to move freely and the functional groups and the template molecules were completely located in the central area of the bulk/particular polymer layer, it is extremely difficult to extract the original templates so that the MIPs showed high selectivity but weak binding ability, poor site approachability [31,32]. Therefore, surface imprinting technique which is controlling template molecules to locate in the proximity of the surfaces of particles is extremely significant to improve site accessibility and create more available recognition sites. Recently, MIPs-based QDs sensors have been widely studied and reported because of their high selectivity (MIPs) and excellent optical property (QDs) [33–39]. Xu' group has prepared MIPs-based QDs sensor via sol-gel process with dummy template for the sensing of 2,4,6-trinitrotoluene (TNT) [36]. Ren' group has synthesized a novel MIPs-based QDs sensor via precipitation polymerization with ZnS QDs for the detection of cyphenothrin [37]. Moreover, our group has used a polymerizable surfactant Octadecyl-4-vinylbenzyl-dimethyl-ammonium chloride (OVDAC) to modify the surface of QDs and prepared two kinds of MIPs-based QDs sensors for determination of  $\lambda$ -cyhalothrin [38] and bifenthrin [39]. Inspired by these important reports, we expect to construct a novel MIPs-based QDs sensors that can selectively recognize and tightly bind SAs.

In this work, we develop a custom-tailored strategy via a surface functional monomer-directing and functional fluorescent material-directing prepolymerization system to form MIPs layers on the surface of SiO<sub>2</sub> sphere. As we know, silica particles are attractive substrates for the synthesis of composite material due to the chemical stability, numerous hydroxyl groups and biocompatibility [40–43]. In this unique synthetic process, the modified SiO<sub>2</sub> sphere, modified QDs, SAs, acrylamide (AM), and ethyl glycol dimethacrylate (EGDMA) were used as the supporter, the fluorescent material, the template molecule, the functional monomer, and the cross-linker, respectively, and the obtained composite materials (MIPs/QDs@SiO<sub>2</sub>) were prepared by a two-step polymerization process. The morphology, shape, size, characteristic, optical stability, performance of the MIPs/QDs@SiO<sub>2</sub> were investigated. The experimental data exhibit that MIPs/QDs@SiO<sub>2</sub> as specific sensors have highly selectivity for quantitative analysis of trace SAs. Finally, this novel sensor was used as an efficient tool for the determination of SAs in real samples. The objective of this study is to develop a kind of high-performance fluorescent composite sensors for the selective detection of SAs.

## 2. Experimental

### 2.1. Materials and chemicals

All chemicals used in the synthetic process were of at least analytical grade. Octadecyl-4-vinylbenzyl-dimethyl-ammonium chloride (OVDAC) was purchased from TCI (Shanghai) Development Co., Ltd. Tetraethoxysilane (TEOS), aminopropyltriethoxysilane (APTES), acryloyl chloride, thioglycolic acid (TGA) (98%), CdCl<sub>2</sub>·2.5H<sub>2</sub>O (99.99%), NaBH<sub>4</sub> (99%), tellurium powder (99.99%), acrylamide (AM), ethylene glycol dimethacrylate (EGDMA), 2,2'-azobis (2-methylpropionitrile) (AIBN), sulfadiazine, sulfamethyldiazine, sulfadimidine, sulfamethoxazole, artemisinin, erythromycin, terramycin and 2,6-dichlorophenol were all purchased from Aladdin reagent Co., Ltd. (Shanghai, China). Chloroform, ethanol, sodium hydroxide and ammonia solution (25–28%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Double distilled water (DDW) was used throughout the experimental procedures.

### 2.2. Instrument

The fluorescence measurements were performed with a Cary Eclipse spectrofluorometer (USA) equipped with a plotter unit and a quartz cell. The sizes and morphologies of prepared samples were obtained by transmission electron microscope (TEM, JEOL, JEM-2100).

### 2.3. Synthesis and surface modification of SiO<sub>2</sub>

SiO<sub>2</sub> particles were fabricated by the Stöber method. 49.5 mL of DDW, 32.4 mL of ethanol, and 18 mL of ammonia solution were added in a 500 mL round bottom flask and vigorously stirred. Then 9.0 mL of TEOS and 91 mL of ethanol was quickly added to the mixture. The above solution was stirred at room temperature for 2.5 h. The products were centrifuged and washed with DDW. Finally, the obtained SiO<sub>2</sub> particles were dried in vacuum oven at 60 °C for further use.

The surface of SiO<sub>2</sub> particles was endowed with reactive vinyl groups through modification with acryloyl chloride. Normally, 0.5 g of SiO<sub>2</sub> particles and 1.0 mL of APTES were dispersed into 50 mL of dry toluene and forcibly stirred under N<sub>2</sub> at 90 °C for 24 h. Then the products were centrifuged and washed with ethanol three times. The obtained products were dried in vacuum oven at 60 °C overnight. Subsequently, 0.1 g dry K<sub>2</sub>CO<sub>3</sub> and 0.5 g the anhydrous products were dispersed into 50 mL dry toluene, and rapidly added 3.0 mL acryloyl chloride, magnetic stirring under N<sub>2</sub> at 90 °C for 24 h. Finally, the AM-APTES-SiO<sub>2</sub> were obtained and dried under vacuum for further use.

### 2.4. Synthesis and chemical modification of CdTe QDs

The synthesis and chemical modification of CdTe QDs were carried out according to previous reports [38]. Briefly, the freshly NaHTe solution was rejected to a mixed solution containing CdCl<sub>2</sub> and TGA in a bath magnetic stirring. Then the mixture was refluxed at 100 °C for 2.0 h under N<sub>2</sub> atmosphere, and then the stable water compatible CdTe QDs with green fluorescence were obtained and used in the following experiments. The obtained CdTe QDs were mixed with OVDAC for 2.0 h. Then the chloroform was added to the mixture solution, and the OVDAC modified CdTe QDs (OVDAC/CdTe QDs) were obtained.

### 2.5. Synthesis of MIPs/QDs@SiO<sub>2</sub>

The high-performance fluorescent SAs imprinted composite sensors (MIPs/QDs@SiO<sub>2</sub>) were synthesized by a two-step imprinting polymerization process [35]. Briefly, 2.5 mg OVDAC/CdTe QDs, 100 mg AM-APTES-SiO<sub>2</sub>, 0.1 mmol of SAs, 0.4 mmol of AM, and 2.0 mmol of EGDMA were dispersed in 60 mL acetonitrile to self-assemble at room temperature. Next, 10 mg of AIBN as the initiator was added and the mixture was purged with N<sub>2</sub> for 30 min. Finally, the slow prepolymerization was started at 50 °C for 6.0 h and the normal polymerization was completed at 60 °C for 24 h. After the reaction, the resulting MIPs/QDs@SiO<sub>2</sub> were collected by centrifugation and washed with ethanol several times to remove the unreacted monomers, and the templates in the MIPs/QDs@SiO<sub>2</sub> were also removed with the ethanol via the extraction method. The molecularly non-imprinted composite sensors (NIPs/QDs@SiO<sub>2</sub>) were also fabricated under the same condition but without the addition of SAs.

### 2.6. Measurement procedure

The fluorescent composite materials were dispersed in DDW to obtain the fresh-made stock solution (500 mg/L). SAs were dis-

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