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Novel monodisperse molecularly imprinted shell for estradiol based on surface imprinted hollow vinyl-SiO₂ particles

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ABSTRACT

A novel monodisperse molecularly imprinted shell was prepared based on surface imprinted hollow vinyl-SiO₂ particles and applied to selective recognition and adsorption of estradiol (E₂). This method was carried out by introducing vinyltriethoxysilane to the surface of polystyrene (PS) spheres by a simple one-step modification, followed by dissolution to remove the PS cores, and then by copolymerization of functional monomers *via* surface imprinted on the hollow vinyl-SiO₂ particles to prepare uniform E₂-imprinted shells. Two interesting characteristics were found: first, the obtained hollow molecularly imprinted polymer shells (H-MIPs) had highly monodispersity, uniform spherical shape with a shell thickness of about 40 nm; and then, the method was simple, easy to operate by directing coating of a uniform shell on hollow particles *via* surface imprinting. The resultant H-MIPs demonstrated improvements in imprinting factor and binding kinetics, owing to the high selectivity to template molecules, surface imprinting technique and hollow porous structure. Furthermore, satisfactory recoveries of 97.0 and 94.8% with respective precisions of 2.5 and 2.7% were achieved by one-step extraction when H-MIPs were used for the preconcentration and selective separation of estradiol in milk samples at two spiked levels. The simple, effective H-MIPs based strategy provided new insights into the formation of various functionalized coating layers on different kinds of support materials with versatile potential applications.

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1. Introduction

During recent years, it has been increasingly reported that endocrine disrupting compounds (EDCs) enter the human living environment. These compounds have become a growing concern due to their potential in altering the normal endocrine function and physiological status of humans and animals [1]. Estradiol (17β-Estradiol or E₂), as the most active estrogen, can disrupt vital systems (e.g., the endocrine system) in aquatic organisms and increase the risk of cancer [2,3]. In order to prevent the uncontrolled effects on the human health and the deleterious effects on the aquatic environment, the development of highly effective and

practicable methods for the selective recognition, determination and removal of trace residues of E₂ is urgently required.

Molecularly imprinting is known as a technique for the generation of polymer-based molecular recognition elements tailor-made for a given target or a group of target molecules [4–6]. The resulting molecularly imprinted polymers (MIPs) not only possess desired binding properties, selectivity and specificity for target molecules, but also exhibit far greater physical robustness and thermal stability. These characteristics allow MIPs to be used in a wide range of fields, such as separation, sensors, catalysis and drug delivery [7–11]. However, the MIPs prepared by traditional methods have met with many limitations including incomplete template removal, small binding capacity, low affinity, and irregular materials' shape. One of main reasons is that the removal of template molecules located at interior area of bulk materials is quite difficult due to the high cross-linking nature of MIPs [12]. Recently, the synthesis of core-shell-type MIPs has provided a convenient and controllable approach for preparing MIPs, due to

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its intrinsic advantages, such as good dispersion, rapid binding kinetics, easy and complete removal of template molecules [13–15]. Monomer-directing polymerization [12] and layer-by-layer deposition [16] protocols for highly dense imprinting of 2,4,6-trinitrotoluene on the surface of silica nanoparticles are developed. These techniques have been widely adopted for producing core-shell MIP microspheres. Although the method to obtain core-shell imprinted microspheres possesses remarkable advantages, the resultant products often have a low rebinding capacity [17], since the solid cores do not generate recognition cavities and possess most mass of the imprinted materials, which decreases the binding capacity per unit mass of MIPs.

To solve these problems, recently, our group has begun to explore alternative approaches by combining molecular imprinting technology with hollow polymer preparation methods [18,19]. Several types of hollow porous MIPs were prepared by multistep seed swelling polymerization, and were applied as solid-phase extraction sorbents for selective preconcentration and specific recognition of triazines in soil samples [18] and Sudan I in chili sauce samples [19]. The main advantages recognized up to now in the use of hollow polymers can be attributed to their controllable pore and hole structures, which favors mass transfer.

Inspired by these studies, now, we aspired to extend the hollow molecularly imprinting polymer preparation methods to the direct coating of a uniform shell on hollow particles via surface imprinting. Vinyltriethoxysilane (VTES) as a precursor was first introduced to the surface of polystyrene (PS) spheres by a simple one-step modification, followed by dissolution to remove the PS cores, and thus by copolymerization of functional monomers on hollow vinyl-SiO₂ particles to prepare uniform E₂-imprinted polymer shells. The developed approach could supply great application potentials not only in molecular imprinting fields, but also in the preparation of various functional coating layers on PS support.

2. Experimental

2.1. Materials and instruments

2-(Methacryloyl)ethyl trimethylammonium chloride (MTC) aqueous solution, vinyltriethoxysilane (VTES), E₂, estriol (E₃), diethylstilbestrol (DES), methacrylic acid (MAA), and ethyleneglycol dimethacrylate (EGDMA) were purchased from Sigma-Aldrich and used as received. Styrene (St) was purchased from Sigma-Aldrich and purified by washing with NaOH and ultrapure water. 2,2'-Azobis-isobutyronitrile (AIBN) was obtained from Shanghai Chemical Reagents Company (Shanghai, China) and recrystallized in methanol prior to use. Polyvinylpyrrolidone (PVP), tetrahydrofuran (THF), and aqueous ammonia solution were supplied by Tianjin Reagent Plant (Tianjin, China). High performance liquid chromatography (HPLC) grade acetonitrile (ACN) was purchased from Merck (Darmstadt, Germany). Deionized water used throughout the work was produced by a Milli-Q Ultrapure water system with the water outlet operating at 18.2 MΩ (Millipore, Bedford, MA, USA).

FT-IR analyses were carried out by a FT-IR spectrometer (Thermo Nicolet Corporation, USA). The morphological evaluation was observed by TEM (JEM-1230, operating at 100 kV) and SEM (JSM 5600 LV, operating at 20 kV). The specific surface areas and pore sizes of the polymers were measured via Brunauer–Emmett–Teller (BET) analysis by nitrogen adsorption experiments. The measurement was operated on AUTOSORB 1 (Quantachrome Instruments, Germany). The samples were degassed at 250 °C in vacuum prior to adsorption measurements. Thermogravimetric (TG) analysis about thermostability and purity was performed by a ZRY-2P thermal analyzer (Mettler Toledo).

2.2. Preparation of PS support particles

The monodisperse positively charged PS particles were prepared by dispersion polymerization as described [20] with necessary modifications. Briefly, 6 mL St, 1.5 g PVP, 0.2 g AIBN, 5 mL H₂O and 29 mL ethanol were charged into a 250 mL three-necked flask. The mixing solution was deoxygenated by bubbling nitrogen gas at room temperature for 30 min, and was then heated to 70 °C with vigorous magnetic stirring for 1.5 h, followed by addition of 6 mL St, 29 mL ethanol and 0.39 g MTC. Then the reaction was carried out under vigorous magnetic stirring at 70 °C for 24 h.

2.3. Synthesis of hollow vinyl-SiO₂ spheres

The obtained PS suspension was cooled to 50 °C, and 3 mL ammonia was then added and the mixture was stirred for 5 min. 9 g VTES was added dropwise to the suspension and the mixture reacted at 50 °C for around 5 h with constant stirring. The monodisperse PS@vinyl-SiO₂ core-shell particles were obtained. Then the particles were separated from the reaction medium by centrifuging, and then were washed several times with ethanol. After removing the PS cores by dissolution in THF, the hollow vinyl-SiO₂ spheres were attained.

2.4. Molecular imprinting on the surface of hollow vinyl-SiO₂ spheres

Typically, hollow vinyl-SiO₂ spheres (50 mg) were dispersed in 50 mL of ACN by ultrasonication. E₂ (68 mg, 0.25 mmol), MAA (85 μL, 1 mmol), EGDMA (945 μL, 5 mmol) and AIBN (20 mg) were then added into the above solution followed by purging with nitrogen for 30 min. A two-step temperature-rising polymerization reaction was carried out in a water bath at 50 °C for 8 h, followed by 60 °C for 24 h. The resultant polymer shells were separated and washed with methanol/acetic acid solution (9:1, v/v) to remove both the template molecules and residual monomers. Finally, the polymer shells were dried to constant weight under vacuum at 40 °C. For comparison, solid molecularly imprinted polymers were prepared in the same manner but without removing the PS cores, namely S-MIPs for simplicity. As a control, their corresponding non-imprinted polymers (NIPs) were prepared under identical conditions but omitting the template in the reaction system.

2.5. Adsorption property investigation of the H-MIPs

The adsorption experiments were carried out as follows: 20 mg polymers were dispersed in a 5 mL flask containing 2.0 mL E₂ solutions of various concentrations. After 24 h of shaking at room temperature, the samples were centrifuged. The amount of E₂ adsorbed onto the imprinted polymer shells was determined by measuring the difference between total E₂ amount and residual amount in solution with HPLC-UV. Meanwhile, the binding kinetics was detected by monitoring the temporal amount of E₂ in the solutions at regular times. Selectivity experiments were made by using E₃ and DES as structural analogs.

2.6. Analysis of E₂ in milk samples

The milk samples analyzed were obtained from local markets. 30 mL ACN was added to 10 mL of milk sample and the mixture was shaken vigorously for 15 min. Thereafter, the mixture was centrifuged at 4500 rpm for 30 min. For spiked tests, appropriate amounts of E₂ standard were added into the milk sample and extracted from the matrix through the overall procedure, at levels of 10 and 100 μg L⁻¹, respectively. H-MIPs of 100 mg were dispersed in 5 mL blank or spiked solutions and incubated for

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