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Molecular bottlebrush polymer modified magnetic adsorbents with high physicochemical selectivity and unique shape selectivity

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ABSTRACT

A molecular bottlebrush functionalized magnetic adsorbent (magGO@bottlebrush) was fabricated in this work. Poly(hydroxyethyl methacrylate) (PHEMA) was first grafted from polydopamine coated magnetic graphene oxide *via* surface-initiated atom transfer radical polymerization (SI-ATRP) to produce the backbone of the molecular bottlebrush. Further modification was followed by grafting poly(styrene) *via* a second SI-ATRP from the PHEMA chains to yield the magGO@bottlebrush. Multiple interactions including hydrophobic, π-π stacking and π-π electron-donor-acceptor interactions greatly contributed to the solute retention. The adsorbent possessed unique shape selectivity, it provided high affinity to non-planar and non-linear compounds. Profiting from densely grafted phenyl and carbonyl groups on the adsorbent, multivalent interactions were exploited to enhance the selectivity for analytes with multiple recognition motifs. Bisphenol A (BPA) was chosen as a model analyte to test real applications of the adsorbent, considering its structural features. The adsorbent owns high adsorption capacity to BPA, and can be readily used for rapid and efficient enrichment of trace BPA from water samples.

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1. Introduction

High selective separation media are the key for high efficient isolation and enrichment of target molecules from complex samples, their design and preparation have always been the hot topics in separation science. Molecular recognition processes in biosystems are important sources for developing high selective separation media. Multivalent interaction is a common molecular recognition phenomenon in biological systems. It means that multiple ligands on one object simultaneously bind to multiple receptors on another object [1], such as antibody-antigen interaction, virus-cell binding. In recent years, multivalent interactions have been extensively studied, the results show that the binding strength of the multivalent interaction is orders of magnitude over the monovalent interaction and gives a superselectivity [2–4]. Attachment of multiple identical ligands to a polymer backbone is a common method for constructing multivalent ligands [5], known as polymeric multivalent ligands.

Polymeric multivalent ligands have been introduced into preparation of high selective adsorbents. Poly(amidoamine) (PAMAM) dendrimer [6,7] and branched polyethyleneimine (PEI) [8] have been used as scaffolds to amplify the number of recognition moieties and to yield multivalent ligands. Polymeric multivalent ligands have also been modified on solid substrates by using surface-initiated atom transfer radical polymerization (SI-ATRP) technique [9,10]. All these results indicate that multivalent ligands can afford adsorbents with high selectivity. However, up to date, multivalent ligands are mainly utilized to fabricate adsorbents for separation of biopolymers such as proteins or peptides. There are rare reports to introduce multivalent ligands for adsorption and separation of small organic molecules.

Molecular bottlebrush (also known as molecular brush, bottlebrush) is a type of branched polymers, they have one or more polymeric side chains attached to each repeat unit of a linear polymer backbone, leading to a very high side chain density [11,12]. Steric repulsions between the densely grafted side chains force the backbone and the side chains to adopt highly extended chain conformations [11–15], and promote chain ordering, especially when anchored on surfaces. Reuter et al. have found that the bottlebrush-shaped sialic acid polymer had much higher affinity to influenza virus than the linear- and PAMAM dendrimer-shaped ones, the affinity was 50000-fold of single sialic acid [16]. Therefore, it can be expected that highly selective adsorbents can be obtained by densely grafting molecular bottlebrushes pendant with numerous ligands onto substrates.

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The term "shape selectivity" is commonly used to describe a chromatographic quality of certain stationary phases to recognize and separate certain geometric isomers based on their molecular shape, rather than other physical or chemical differences of the solutes [17]. In order to avoid confusions, we arbitrarily define the usual sense of selectivity as "physicochemical selectivity", *i.e.* the capability to discriminate substances based on their physical or chemical differences. In this paper, the common "selectivity" means "physicochemical selectivity" except that it appears in the phrase "shape selectivity". Shape selectivity has been found to be important in separation of polycyclic aromatic hydrocarbons (PAHs) and their derivatives. Planar and nonplanar molecular shapes usually coexist within these species. There are many reports on developing stationary phases with shape selectivity. Up to now, it has been concluded that the following factors are favorable to increase shape selectivity: polymeric alkyl chain stationary phases [17], longer alkyl chain length [18], higher ligand densities and more ordered chain conformation [19–26]. To date, the previously reported reversed phase materials exclusively have better shape selectivity for planar molecules over nonplanar ones. However, some very important analytes have nonplanar conformations, such as bisphenol A (BPA) [27] and polychlorinated biphenyls (PCBs) [28]. Therefore, to explore reversed phase materials with high shape selectivity for nonplanar molecules are highly expected.

Polydopamine (PDA) can be coated easily on various substrates, and has been extensively used in preparation of new adsorbents to facilitate the surface modification [29–33]. In the present work, a molecular bottlebrush polymer functionalized magnetic adsorbent (magGO@bottlebrush) was prepared based on PDA coated magnetic graphene oxide (magGO@PDA) for the first time. Molecular bottlebrushes were adopted to provide multivalent ligands and make the dense ligands highly ordered, producing high physicochemical selectivity and unique shape selectivity. The interactions responsible for solute retention, shape selectivity, and multivalent interaction for affinity enhancement were investigated in detail. And the magnetic adsorbent was used for preconcentration of BPA from water samples *via* magnetic solid phase extraction (MSPE).

2. Experimental

2.1. Fabrication of the bottlebrush functionalized adsorbents

Hydrophobic bottlebrushes pendant with numerous phenyl rings were grafted from the magGO@PDA, and the synthetic procedures are shown in Fig. 1. Graphene oxide (GO) was prepared by the modified Hummers' method [34], then Fe_3O_4 particles were deposited on the GO by a simple one-step solvothermal method to produce magnetic GO (magGO). After that PDA was coated on the surface through the self-polymerization of dopamine in alkaline buffer at room temperature to facilitate anchoring the initiator [35–37]. The detailed synthetic procedures for preparation of magGO@PDA are described in the Supplementary Information.

2.1.1. Grafting poly(2-hydroxyethyl methacrylate) from the magGO@PDA

The SI-ATRP initiator, 2-BiBB, was coupled to the surface of the magGO@PDA according to the previous method with minor modification [38], the detailed procedures are described in the Supplementary Information. Then poly(hydroxyethyl methacrylate) (PHEMA) was grafted from the magGO@PDA to produce the backbone of the bottlebrush. Detailedly, 0.4 g of the initiator functionalized magGO@PDA was dispersed into 10 mL dried *N,N'*-dimethylfomamide (DMF) containing 2-hydroxyethyl methacrylate (HEMA) (2.4 mL) and 2,2'-bipyridine (Bpy) (123 mg). Then the system was degassed by two freeze-pump-thaw cycles,

after that cuprous bromide (CuBr, 56.80 mg) was added into the vessel, and the mixture was degassed again. The reaction was heated to 70 °C and kept for 16 h under nitrogen atmosphere. After the polymerization was stopped, the materials were washed with DMF, methanol and water in sequence, each for three times. Then the product was dispersed in 40 mL of methanol-0.25 mol L^{-1} Na$_2$EDTA solution (1:1, *V/V*) at 40 °C for 4 h to remove the residual copper ions. Finally, the precipitates were separately rinsed with methanol and water for several times and dried in vacuum overnight. The product is denoted as magGO@PHEMA.

2.1.2. Grafting polystyrene from the magGO@PHEMA

2-BiBB was coupled to the magGO@PHEMA to produce the initiator functionalized backbone, magGO@PHEMA-Br, as described in the Supplementary Information. 2.0 g of the magGO@PHEMA-Br, 1.19 g of Bpy and 20 mL of styrene were dissolved in 10 mL of anisole. Then the system was degassed by two freeze-pump-thaw cycles, after that CuBr (0.54 g) was added into the mixture, and the mixture was degassed again. The polymerization was carried out at 90 °C for 3 h under nitrogen atmosphere and the obtained product was washed with anisole, methanol and water in sequence, each for three times. The subsequent procedures are the same as those described in Section 2.1.1. The final product is denoted as magGO@bottlebrush.

2.2. Sample preparation and MSPE procedures for BPA

The fresh tap water was collected from our laboratory. The commercial bottled water was purchased from a local market, and was heated at 80 °C for 5 h to obtain the heated bottled water. The river water was collected from the moat of Xi'an, at a spot nearby Zhuque Gate. Before use, all the water samples were filtered through 0.45 μm membranes and stored in amber glass containers at 4 °C.

The MSPE was carried out as follows: 10 mg of the adsorbents were dispersed in 10 mL of the sample solution. Then the mixture was gently shaken for 3 h at 25 °C. And then, the adsorbents were isolated rapidly from the aqueous solution by an external magnet and the supernatant was decanted away. Subsequently, the adsorbents were rinsed with distilled water, and then dispersed in 1 mL methanol with continuous vibration for 30 min to desorb the analyte. Finally, the eluate was dried under a stream of nitrogen gas in a water-bath at 35 °C using a MV5 automatic multi-sample concentrator, and re-dissolved with 200 μL methanol-water (70/30, *V/V*) before HPLC analysis.

2.3. Chromatographic conditions

All the chromatographic measurements were performed on a Shimadzu Prominence LC-20 A chromatograph (Tokyo, Japan), equipped with a RF-10A XL fluorescence detector. 20 μL of samples were injected into an InertSustain® C18 column (250 mm × 4.6 mm i.d., 5 μm) for analysis. The mobile phase is 30% methanol aqueous solution, and flow through the column at a flow rate of 1.0 mL min^{-1}. The chromatograms were traced by fluorescence response at an emission wavelength at 304 nm, with an excitation wavelength at 278 nm.

3. Results and discussion

3.1. Preparation of the molecular bottlebrush polymer grafted adsorbent

As mentioned above, selectivity is very important for adsorbents. However, selectivity is usually quite difficult to adjust once the ligands are fixed. Reverse-phase adsorption materials have