



# Grafting molecularly imprinted poly(2-acrylamido-2-methylpropanesulfonic acid) onto the surface of carbon microspheres

Yongzhen Yang<sup>a,b</sup>, Yan Zhang<sup>a,c</sup>, Sha Li<sup>a,c</sup>, Xuguang Liu<sup>a,c,\*</sup>, Bingshe Xu<sup>a,b</sup>

<sup>a</sup> Key Laboratory of Interface Science and Engineering in Advanced Materials, Taiyuan University of Technology, Ministry of Education, Taiyuan 030024, China

<sup>b</sup> Research Center on Advanced Materials Science and Technology, Taiyuan University of Technology, Taiyuan 030024, China

<sup>c</sup> College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

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## ABSTRACT

Poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) was grafted on the surface of carbon microspheres (CMSs), which were modified in prior by a mixed acid (HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>) oxidation and 3-methacryloxypropyl trimethoxysilane silanization. Then, the molecularly imprinting polymerization was carried out towards the macromolecule PAMPS grafted on the surface of CMSs using dibenzothio-*phene* (DBT) as template, ethylene dimethacrylate as cross-linking agent and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (APS) as initiator to prepare surface molecularly imprinted polymer (MIP-PAMPS/CMSs) for adsorbing DBT. The optimized conditions of grafting PAMPS, including AMPS dosage, APS content, reaction temperature and reaction time, were emphasized in this paper. The morphology of the samples was characterized by field emission scanning electron microscopy. The functional groups were analyzed qualitatively by Fourier transform infrared spectrometry. The grafting degree of PAMPS was investigated by thermogravimetry. The results show that the preferable AMPS dosage, APS content, reaction temperature and time were 5 g, 0.15 g, 70 °C and 12 h, respectively, for preparing PAMPS/CMSs composite on the basis of 1.0 g of silanized-CMSs. The adsorbing characteristic of MIP-PAMPS/CMSs toward DBT was studied preliminarily with dynamic adsorption. In the experiment of dynamic adsorption, MIP-PAMPS/CMSs and non-imprinted polymer (NIP-PAMPS/CMSs) were compared with respect to their rapid adsorption in 1 mmol/L of DBT solution in *n*-hexane. When the first 1 mL of 1 mmol/L DBT solution was injected and flowed through a column packed with 0.1 g of MIP-PAMPS/CMSs, the content of DBT reduced to 0.265 mmol/L, that is, decreased significantly from 279 to 74 ppm. When 3 mL of DBT solution was flowed through the packed column, the adsorption of MIP-PAMPS/CMSs toward DBT reached saturation with the maximum adsorption amount of  $1.38 \times 10^{-2}$  mmol/g and the overall adsorption efficiency of 46%, while NIP-PAMPS/CMSs adsorbed only  $1.66 \times 10^{-3}$  mmol/g of DBT. It is suggested that the MIP-PAMPS/CMSs had much better adsorption property towards DBT than NIP-PAMPS/CMSs.

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## 1. Introduction

Many types of technique for removing sulfur compounds from fuel have been developed, such as hydrodesulfurization, adsorption by porous materials, catalytic distillation, and biochemical methods [1]. However, these methods suffer from various restrictions as the regulations on SO<sub>2</sub> emission are getting more and more stringent. Molecular imprinting techniques, which allow synthesis of polymers with selectivity towards a predetermined target, have been developed and expected to be a new

desulfurization means [2–5]. Molecularly imprinted polymers (MIP) are prepared by copolymerizing a monomer with a cross-linker in the presence of a template molecule. After the polymerization, the template is removed from the porous network by washing and cavities in the polymeric matrix are left to be complementary to the template in size, shape and chemical functionality. The main limitations in traditional molecular imprinting technology are its low selectivity, low response kinetics and large template size. So the surface molecular imprinting technique has been explored by grafting a very thin polymer film onto a support, such as polymer beads [6], silica-based materials [7,8] and carbon nanotubes [9–12]. This technique improves the binding rate between recognition sites and imprinted molecules, and correspondingly the adsorption efficiency of the molecularly imprinted materials, by designing the molecular recognition sites on the surface of imprinted materials. Because of their large surface area, good

\* Corresponding author at: College of Chemistry and Chemical Engineering, Taiyuan University of Technology, 79 West Yingze Street, Taiyuan 030024, China. Tel.: +86 351 6014138; fax: +86 351 6014138.

E-mail addresses: [liuxuguang@tyut.edu.cn](mailto:liuxuguang@tyut.edu.cn), [yyztyut@126.com](mailto:yyztyut@126.com) (X. Liu).

chemical, mechanical and thermal stabilities [13], carbon microspheres (CMSs) are promising support for surface imprinting [1]. However, the surface functionalization of CMSs for molecular recognition can only be achieved by a multiple-step process of surface activation, oxygen bridging, polymer grafting and cross-linking. In our previous study [1], MIP on the surface of CMSs for adsorbing dibenzothiophene (DBT) template was obtained with methacrylic acid as functional monomer. A strong intermolecular force between functional monomer and template is needed in the preparation of MIP with stable template-monomer composites and excellent properties. In this paper, 2-acrylamido-2-methylpropanesulfonic acid (AMPS), in which  $-\text{SO}_3\text{H}$  group has strong polarity to combine DBT molecule through electrostatic interaction and hydrogen bond, was selected as the monomer to prepare stable composites of template and functional monomer. AMPS can be dissolved in water well to realize aqueous polymerization to give a thermally stable polymer with decomposition temperature of  $210^\circ\text{C}$ . The effectiveness of MIP greatly depends on the content of the monomer grafted onto the surface of CMSs [14]. Therefore, the influences of monomer dosage, initiator content, reaction temperature and reaction time were discussed for grafting reaction. The dynamic adsorption of molecularly imprinted poly AMPS on the surface of CMSs (MIP-PAMPS/CMSs) towards DBT was also investigated preliminarily.

## 2. Experimental

### 2.1. Materials

CMSs with about 350 nm in diameter were synthesized by chemical vapor deposition with  $\text{C}_2\text{H}_2$  as carbon source and Ar as carrier gas [15]. 3-Methacryloxypropyl trimethoxysilane (KH-570,  $\geq 95$  wt%),  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (APS,  $\geq 99.5$  wt%) and chloroform ( $\geq 99$  wt%) were provided by Tianda Chemical Reagent Company, Tianjin, China. Ethylene dimethacrylate (EDMA, 98 wt%) and AMPS (99 wt%) were purchased from Alfa Aesar, USA. All other chemicals were of analytical grade and employed as received. Distilled water was used to prepare all buffers and other solutions.

### 2.2. Oxidation of CMSs

Firstly, the as-prepared CMSs were treated in ethanol by ultrasonic vibration to obtain purified CMSs. To improve the surface activity of purified CMSs, oxygen-containing polar groups were introduced onto the surface of CMSs by acid oxidation. After adding 1.0 g of CMSs to the mixed acid of 30 mL of  $\text{HNO}_3$  (65 wt%) and 90 mL  $\text{H}_2\text{SO}_4$  (96 wt%) in a flask, the mixture was ultrasonicated at  $70^\circ\text{C}$  for 1 h, filtered, washed with distilled water several times until the pH value approached to neutrality, and then dried at  $40^\circ\text{C}$  in air to give oxidized-CMSs.

### 2.3. Silanization of oxidized-CMSs

As shown in Scheme 1, C=C bond was introduced onto the surface of oxidized-CMSs by silanization with coupling agent KH-570 in order to further increase the reactivity of CMSs surface. Oxidized-CMSs (0.3 g) were added to 60 mL of a mixed solvent of ethanol and water ( $v/v = 3:1$ ), followed by the addition of 1 mL of KH-570. The mixture was refluxed in  $\text{N}_2$  atmosphere at  $65^\circ\text{C}$  for 2 h under magnetic stirring. Then the samples were extracted with ethanol repeatedly to remove excess KH-570 and dried at  $50^\circ\text{C}$  for 24 h, resulting in the formation of silanized-CMSs.

### 2.4. Preparation of PAMPS/CMSs composite

PAMPS was grafted onto the surface of silanized-CMSs using APS as initiator in water under  $\text{N}_2$  atmosphere, as shown in Scheme 2. The C=C bonds in AMPS and on the surface of CMSs were opened under the initiation of APS, and then linked to each other. After coupling and polymerization, PAMPS was grafted onto the surface of silanized-CMSs.

A typical grafting process was as follows: a certain amount of AMPS was dissolved in 10 mL of distilled water under stirring, and transferred to a 250 mL three-neck flask with 0.2 g of silanized-CMSs. The mixture solution was stirred under  $\text{N}_2$  atmosphere at the given temperature, followed by addition of a certain amount of APS dissolved in 10 mL of distilled water in a given period of time. After cooling, the samples were washed successively by distilled water to remove the polymer physically adhered on the surface of CMSs, and dried in vacuum to obtain PAMPS/CMSs. The influences of AMPS dosage, APS content, reaction time and reaction temperature were investigated.

### 2.5. Preparation of imprinted material MIP-PAMPS/CMSs

As shown in Scheme 3, PAMPS absorbed DBT by the intermolecular hydrogen bond and electrostatic interaction, and fixed DBT in the network with EDMA as cross-linking agent. After cross-linking reaction, the templates were removed from the porous network by washing, and cavities in the polymeric matrix were left, which are complementary to the template in size, shape and chemical functionality.

A typical imprinting process consisted of a complex procedure. DBT (0.111 g) was dissolved in 10 mL of chloroform in a three-neck flask. Then, 0.1 g of PAMPS/CMSs was added under stirring for 30 min to combine DBT, followed by the addition of 3 mL of EDMA. The mixture solution was refluxed at  $50^\circ\text{C}$  for 10 h. Afterwards, the samples were washed successively by the mixed solvent of methanol and acetic acid ( $v/v = 9:1$ ) to remove DBT. Ethanol was then used to remove the residual acetic acid. After drying, MIP-PAMPS/CMSs were obtained. For comparison, non-imprinted CMSs (NIP-PAMPS/CMSs) were also prepared in the same way except for the addition of DBT.

### 2.6. Structural characterization

The morphology and structure of the products were characterized by field emission scanning electron microscopy (FESEM, JSM-6700F, operated at 10 kV) with X-ray energy dispersive spectroscopy (EDS), Fourier transformation infrared spectroscopy (FTIR) and thermogravimetry (TG, Netzsch TG 209 F3, in  $\text{N}_2$  atmosphere at heating rate of  $10^\circ\text{C}/\text{min}$ ).

### 2.7. Dynamic adsorption experiment

A packed column for DBT adsorption was prepared by filling 0.1 g of MIP-PAMPS/CMSs or NIP-PAMPS/CMSs into a 10 mL glass column. Dynamic adsorption of DBT was performed at room temperature in the following steps: (1) packed materials were completely soaked by n-hexane; (2) 1.0 mL of 1 mmol/L DBT solution in n-hexane was added in packed column, and the effluent was collected using a weighing bottle; (3) 0.2 mL of effluent was injected into a 10 mL volumetric flasks, and diluted to volume with n-hexane, then concentration of DBT was determined from ultraviolet visible absorption at 237 nm; (4) steps (2, 3) were repeated till the concentration of DBT in effluent approached 1 mmol/L, which suggests the saturated adsorption of DBT.

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