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# The synthesis of hydrophilic molecularly imprinted polymer microspheres and their application for selective removal of bisphenol A from water

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ABSTRACT

The adsorptive materials which have the function of molecular recognition are becoming important as the fast emerging environmental requirements for the analysis and repair of target contaminants present at low concentrations in aqueous matrices. Here, we demonstrate a Pickering emulsion polymerization strategy to build bisphenol A (BPA) imprinted poly(methacrylic acid) microspheres without the traditional organic surfactant. In the synthesis, the only stabilizer is silica particles derived from Stöber process. The molecularly imprinted polymer microspheres were prepared by radical polymerization in the Pickering oil/water emulsion. Both the solid stabilizers and the molecular templates were conveniently removed from the microspheres. The obtained microspheres are of regularly spherical structures and hydrophilic surfaces. The formation of molecularly imprinted sites on the microspheres was validated by the excellent recognition capability toward BPA in the rebinding and competitive binding experiments.

## 1. Introduction

Emerging contaminants are now much concerned because of the potential health and environmental effects. One example is bisphenol A (BPA), a widely used plasticizer for the production of polycarbonate plastics and epoxy resins, which is a kind of mimicking agent that can elicit an estrogenic response [1,2]. Many efforts have been devoted to the detection or removal of BPA from aqueous matrices including food, drinks and surface waters [3–5]. Among them, absorptive polymer microspheres are proved attractive, and have been applied as the adsorbent for purification, the column filler for separation, the enrichment agent for sample pretreatment in analysis [6–8]. However, BPA is always present at very low concentration in complex aqueous matrices like biological samples [9]. Therefore, it would be highly desired for a feasible synthesis of the microspheres with not only uniform sizes for operating convenience and hydrophilic surfaces for water compatibility, but also the molecular recognition abilities to bind with specific target molecules. Moreover, the traditional organic surfactants used in the synthesis should be avoided as possible because their trace residual is proved negative on practical applications and environments [10].

Pickering emulsion, known as an emulsion stabilized by colloidal solid particles, was firstly described by Pickering in 1907 [11]. Until now, remarkable progresses have been made which have been thoroughly reviewed in recent literature [12,13]. Typically, the fine solid particles serving as Pickering emulsifiers are adsorbed at the interfaces between the dispersed and continuous phases [14]. Cheap and nontoxic inorganic particles or polymer colloids like $SiO_2$, $TiO_2$ and polystyrene with properly amphiphilic surfaces are possible to be used for the purpose to substitute the organic surfactants in applications such as wastewater treatment and oil recovery [15–17]. The studies on polymerization in Pickering emulsions (PPE) are also highlighted as a convenient method for the preparation of polymer microspheres.

Molecularly imprinted polymer (MIP) is firstly reported by the groups of Wulff [18] and Mosbach [19]. Over the past years, building artificial molecular recognition systems by MIP technique has attracted tremendous attentions [20–23]. Nevertheless, conventional MIP prepared in organic solvents often exhibit high ratio of non-specific binding when work in aqueous conditions because of the hydrophobic surfaces [24]. In recent studies, the originally hydrophobic surfaces of MIP have been modified by hydrophilic layers, through which the selectivity toward the target molecules in water is improved [25–28]. However, considering on the solvent memory effect, it would be more facile to get MIP with hydrophilic surfaces through the direct polymerization in aqueous medium, for example, PPE in an oil-in-water system [29]. The design is expected to combine both the advantages of MIP and PPE [30]. According to the series reports of Ye and coworkers who used template modified or un-modified silica nanoparticles as the Pickering emulsifier to prepare MIP microspheres, both kinds of

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nanoparticles can lead to MIP through PPE [13,31–33]. But the Pickering emulsifiers used in the above systems have to be either modified or combined with nonionic surfactants [31]. Similarly, in the PPE studies aiming to prepare BPA imprinted microspheres, Chen and coworkers also reported the use of silica nanoparticles as the solid stabilizer [32]. However, the organic surfactant (Triton X-100) was also in the formulations and the spheres showed BPA selectivity only in acetonitrile solutions. Moreover, the functional monomer used to reversibly bind with BPA is 4-vinylpyridine, which is actually expensive and poisonous. Furthermore, the silica nanoparticles have to be removed etching by HF which is hazardous. Up to now, the work on the BPA imprinted polymer spheres suitable to aqueous applications is still lacking.

In this contribution, we report the preparation of poly (methacrylic acid) (PMAA) microspheres containing BPA recognition sites, carboxylic acid rich hydrophilic surfaces and removable Stöber silica particles as the only stabilizer. Aiming to realize the design, a PPE based molecularly imprinting method is proposed, which started from the building of the oil/water Pickering emulsion stabilized by silica particles whose oil phase was composed by commercial methacrylic acid (MAA), BPA, ethylene glycol dimethacrylate, proper porogen and initiator. MAA would bind with BPA based on hydrogen bonding. The binding sites were immobilized by the polymerization and crosslinking of the monomers. After the extraction out of the physically incorporated BPA, its molecular information was imprinted on the polymer spheres. In addition, the emulsifier particles are easy to be washed off from the sphere surfaces. The remained abundant carboxylic acid groups make the spheres hydrophilic enough to be used in aqueous mediums to rebinding with BPA. The whole process is presented in Scheme 1. The advantage for the building of imprinted sites on the spheres is that these sites can recognize the template molecules and selectively bind them through their aqueous solutions. The disturbance of other solute coexisting with BPA by competing absorption would be much suppressed as the mismatched space configuration with the imprinted sites. Thus, only the target BPA is preferred to be bound on the spheres with improved affinity which would be much useful in the enrichment or removal of BPA from complex aqueous matrices. The BPA rebinding capability of the spheres as well as the kinetics is also discussed in the following work.

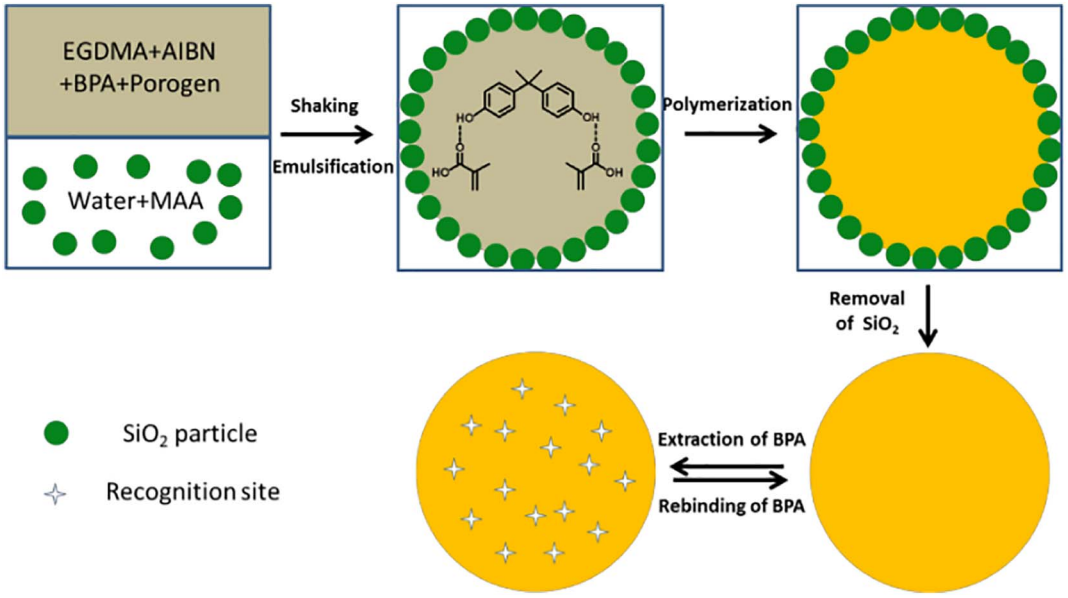
## 2. Materials and methods

### 2.1. Materials

Ethylene glycol dimethacrylate (EGDMA) and acriflavin (AFN) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). Methacrylic acid (MAA), BPA, *p*-tert-butylphenol (BP), hydroquinone (HQ), tetraethyl orthosilicate (TEOS) and azobisisobutyronitrile (AIBN) were purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). Methanol and ammonium hydroxide (25%) were supplied by Beijing Chemical Works (Beijing, China). Other chemicals were of analytical grade and used without further purification. The water used in all the experiments was deionized (DI) water purified by a Milli-Q system (Zhongyang, Beijing, China).

### 2.2. Instruments

The size of emulsion droplets was characterized by the optical microscope (XJZ-1A, COIC). The morphology of MIP microspheres was observed by scanning electron microscope (SEM, VEGA3 SBH, TESCAN). Fluorescence microscope images were inspected with epi-fluorescence microscope (IX81, OLYMPUS). The image of the silica particles was obtained by SEM (S-4700, HITACHI). The number-average diameter of emulsion droplets and microspheres, $\overline{D_n} = \sum n_i d_i / \sum n_i$, was estimated from the optical and SEM images of each sample from about 50 droplets/spheres, respectively. The polydispersity index, $PDI = \overline{D_w}/\overline{D_n}$, was calculated using $\overline{D_n}$ and the weight-average diameter, $\overline{D_w} = \sum n_i d_i^4 / \sum n_i d_i^3$, where $n_i$ is the number of emulsion droplets or microspheres with diameter $d_i$ [33]. The surface area analysis was performed using the Brunauer-Emmett-Teller (BET) nitrogen adsorption method on an instrument (ASAP 2046, Micromeritics). Before the sorption measurements, the samples were outgassed for at least 24 h at 100 °C. The concentration of BPA, BP and HQ was determined by UV–vis spectrophotometer (UV-3150, SHIMADZU). The quantitative peak of BPA, BP and HQ in water was detected at the wavelength of 277 nm, 275 nm and 289 nm, respectively. UV spectra of BPA, BP and HQ in aqueous solution are provided in the Supporting Information (SI) as Fig. S1. The concentration of BPA in binary solution was quantified using a high performance liquid chromatography (HPLC, 1260, AGILENT).




**Scheme 1.** Schematic illustration for the synthesis of MIP microspheres *via* Pickering emulsion polymerization.