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Regular Article

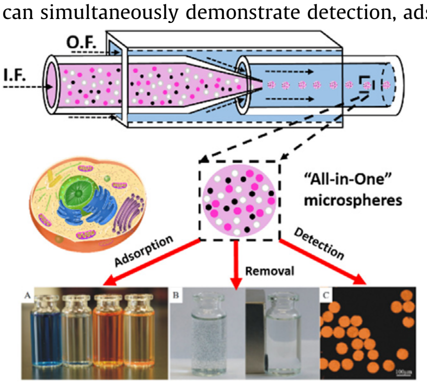
Fabrication of multi-functional porous microspheres in a modular fashion for the detection, adsorption, and removal of pollutants in wastewater

Baojun Ding [a], Jie Wang [a], Shengyang Tao [a,*], Yunzhe Ding [a], Lijing Zhang [a], Ning Gao [b], Guangtao Li [b,*], Haonan Shi [a], Weijun Li [a], Shuo Ge [a]

[a] Department of Chemistry, Dalian University of Technology, Dalian 116024, Liaoning, China
[b] Department of Chemistry, Tsinghua University, Beijing 100084, China

GRAPHICAL ABSTRACT

A novel and convenient method for fabricating high-performance multi-functional materials by integrating the building modules into a single microsphere using the modular fashion assembly methods in a capillary-embedded microfluidic device is presented. The prepared "All-in-One" microspheres can simultaneously demonstrate detection, adsorption and removal of the toxic and hazardous substances, and each function is well performed.



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ABSTRACT

Water pollution control has become significant challenges in recent years because of their extensive species diversity. It is critical to developing general-purpose materials for environmental rehabilitation. In this paper, a novel module-assembly method is developed to prepare multi-functional materials for treating pollutants in water. Building blocks are porous nanoparticles with a different function. Microspheres (MS) with a diameter of 90 μm are prepared and have a coefficient of variation of 6.8%. The modular fashion of self-assembly process in a microfluidic chip is the crucial factor in fabricating the multifunction material. The assembled microspheres with different building modules still have a specific surface area larger than 400 $m^2\ g^{-1}$, and exhibit excellent performance in adsorbing various pollutants in water, such as heavy metal ions and organic dyes. The adsorption capacities of them to Hg^{2+} and orange II reach 150 mg g^{-1} and 333 mg g^{-1}, respectively. The integrated fluorescence probes in microspheres can detect low concentration (9.8 ppb) of Hg^{2+}. Microspheres integrated with Fe_3O_4 nanoparticles have a magnetic susceptibility of 6.01 emu g^{-1} and can be easily removed from wastewater by applying an external magnetic. Due to the stability of inorganic building blocks, each function in the assembled system is well performed, and multi-functional "All-in-One" materials can be easily fabricated.

* Corresponding authors.
E-mail addresses: taosy@dlut.edu.cn (S. Tao), LGT@mail.tsinghua.edu.cn (G. Li).

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1. Introduction

Clean drinking water is one of the major challenges faced by many developing countries. At present, water pollution has brought a severe threat to people's lives and health [1,2]. Chemical industries, metallurgy, printing and dyeing industry, will often bring the discharge of a large number of heavy metal ions, dyes, and other high water-soluble substances. These contaminants can cause a high incidence of cancer, mental illness, reproductive and blood diseases, etc. [3–6]. Purifying sewage and detecting pollutants are both urgent problems in the field of environmental materials [7,8]. Porous materials are one of the most widely used materials for purifying water and sensing hazardous substances. Such as diatomite [9–11], molecular sieves [12–14], activated carbon [15,16], chitosan [17–22], and synthetic resin [23,24]. Conventional adsorbents tend to have a good effect for a particular class of contaminants. However, there is a wide variety of pollutants in the water, including heavy metal ions, inorganic salts, organic molecules and so on [25]. Therefore, it is essential to develop general-purpose adsorbents and sensors with universal applicability. At the same time, materials dispersed in the water also need to be quickly removed after the adsorption of pollutants, to avoid the time and energy waste caused by sedimentation and other separation processes [26,27].

In nature, the microbes with physiological activity have excellent ability to indicate and purify pollutants [28]. Microorganisms are small, but their tiny cells, with the nucleus, mitochondria, and other different organizational structure, perform their duties to maintain a variety of biochemical reactions and complete the physiological activities. Many single-celled organisms can use different organelle secretion of enzymes in the complex components of the wastewater, to achieve the purpose of pollution remediation [29]. From this point we can find that the coexistence of multiple functions, synergy play a role is one of the crucial characteristics of biological systems. Therefore, it is possible to develop high-performance materials with adsorption and detection properties for different pollutants using the artificial method to realize the multi-functional integration. However, the adsorption and recognition sites of different substances cannot coexist in the same system at will, and sometimes they will react with each other. What's more, the integration of different functions in the same material often requires multi-step chemical modification process, which also requires superb experimental technology. Moreover, since the different modification reactions are often carried out in series, the yield of the final synthetic material is not satisfactory. It is well known that in cells, the various enzymes are not merely mixed, but are dependent on the role of different organelles, each organelle plays a modular functional expression while protecting the enzyme, to achieve a biological orthogonal reaction process.

Inspired by this feature, herein, we first prepared different functional nanoparticles as building modules, such as adsorption modules, fluorescent sensing modules, and magnetic modules. Then using natural green polymers as binders, these particles are modularly assembled in microfluidic chips to integrate required multiple functions, including pollutants adsorption, heavy metal ions detection, and magnetic field removal, into a single microsphere. The whole modular assembly process is simple and facile. The prepared multi-functional "All-in-One" materials exhibit excellent performance in adsorption of organic and inorganic ions, detection of Hg^{2+} and removal by a magnetic field.

2. Materials and methods

2.1. Reagents and materials

Cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), ammonia solution (25 wt%), hydrazine hydrate (85 wt%), (3-aminopropyl)trimethoxysilane (98 wt%), (3-mercaptopro pyl)trimethoxysilane (95 wt%) were obtained from Beijing Chemical Reagents Company and were used without further purification. Chitosan with low viscosity (<200 mPa·s) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, PR China. Acetic acid was purchased from Beihua Fine Chemicals Co., Ltd., Beijing, PR China. Glutaraldehyde 50% was purchased from VAS Chemical Co., Ltd., Tianjin, PR China. Rhodamine B, reactive X-3B, Orange II, indigo carmine were used as received from Shanghai Chemical Corporation. Liquid paraffin was bought from Guangfu Fine Chemical of Tianjin Co., Ltd., Tianjin, PR China. The surfactant Abil EM 90 was purchased from Evonik Industries.

2.2. Preparation of various functionalized mesoporous nanoparticles

According to the literature, we first synthesized $-NH_2$, $-SH$ grafted mesoporous silica (MSM) [30], magnetic Fe_3O_4 nanoparticles [31] and fluorescent probes-functionalized mesoporous silica spheres [32] as the building modules.

2.3. Fabrication of multi-functional microspheres

2.020 mL acetic acid is added to 98 mL deionized water to prepare 2.0 wt% acetic acid. Then 1.0 g chitosan is added to the 99.0 g of the prepared 2.0 wt% acetic acid to get 1.0 wt% chitosan aqueous solution. Nanoparticles modules were dispersed in the prepared chitosan aqueous solution (1.0 wt% chitosan) to get a uniform liquid mixture, which was used as the inner phase to form monodispersed droplets. The final content of nanoparticles in the inner phase is controlled to 15 wt%. By controlling the composition and content of the nanoparticle modules, it is possible to fabricate one-module, two-module or three-module multi-functional microspheres. When preparing two-module composite microspheres, SH-M (0.15 g,) and NH_2-M (0.15 g), or SH-M (0.28 g) combined with Fe_3O_4 nanoparticles (0.02 g) dissolved in the aqueous chitosan solution (1.70 g, 1.0 wt%) as the inner phase to prepare two-module microspheres NH_2-SH-MS or Fe_3O_4-SH-MS. In the same way, SH-M (0.14 g), NH_2-M (0.14 g) and Fe_3O_4 nanoparticles (0.02 g) were dissolved in the aqueous chitosan solution (1.70 g, 1.0 wt%) to fabricate three-module microspheres Fe_3O_4-NH_2-SH-MS. Meanwhile, RBH-M (0.14 g), SH-M (0.14 g) and Fe_3O_4 nanoparticles (0.02 g) were assembled to produce three-module microspheres Fe_3O_4-RBH-SH-MS. The outer phase is liquid paraffin containing 0.5 wt% glutaraldehyde and 5.0 wt% non-ionic emulsifier EM 90. The solidification bath is liquid paraffin containing 0.5 wt% glutaraldehyde and 2.0 wt% Span 80. The inner flow is injected into the microchannel and separated into monodispersed droplets by the shearing force of the continuous flow. Thus every droplet contains one module, two-module or three-module. Droplets were collected in solidification bath. The microspheres were washed thoroughly with petroleum ether and ethanol and freeze-dried.

2.4. Adsorption equilibrium experiments

The adsorption behaviors of dyes and heavy metals were characterized as follows. In a typical experiment, 4 mg multi-functional microspheres were placed in 20 mL aqueous solution containing different concentrations (10–100 mg/L) of acid dyes and heavy metals. The dispersion mixtures were shaken at a speed of 250 rpm to equilibrate at 25 °C for 24 h. The methods of calculating the multifunctional microspheres' equilibrium adsorption capacities can be found in the ESI.