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Facile synthesis of novel flowerlike magnetic mesoporous carbon for efficient chlorophenols removal

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ABSTRACT

We present here a novel, low cost and environmental-friendly synthetic strategy for fabricating flowerlike magnetic mesoporous carbon (MMC) microspheres by using silica coated Fe_3O_4 as core, anisotropic layered double hydroxide (LDH) nanocrystals as hard template and dopamine as carbon source, respectively. The resulting MMC spheres has high surface areas (90.3 $m^2\ g^{-1}$), excellent magnetic response (16.99 emu g^{-1}), and large mesopore volume (0.22 $cm^3\ g^{-1}$), as well as good chemical inertness and mechanical stability. The MMC spheres were used to adsorb 2,4,6-trichlorophenol (TCP) from simulated water samples. Experiment results suggest that the adsorption was favorable at acidic pH and increased with the rise of initial TCP concentration and temperature. Kinetic parameters were proved to follow the pseudo-second-order kinetics model and the equilibrium data was more favorable for Freundlich isotherm. The equilibrium absorption capacity was 210 mg g^{-1} at initial TCP concentration of 20 mg L^{-1} and increased to 587 mg g^{-1} when the initial TCP concentration was up to 100 mg L^{-1}, which was much higher than those of other carbon-based adsorbents reported in literature. To the best of our knowledge, this is the first report on the synthesis of flowerlike MMC material by using LDH as template and its application as adsorbent to remove TCP.

1. Introduction

In recent years, mesoporous carbon (MC) materials with excellent textural characteristics, high specific surface area, and good chemical and thermal stability have gained increasing attention [1–4]. Their unique channel network provides a highly opened porous host with easy and direct access for guest species. Despite considerable progress in the synthesis of MC, there is a big issue in the separation of MC from aqueous solution. Conventional solid–liquid methods, including filtration and centrifugation, are time consuming and inefficient. Therefore, magnetically functionalized carbon materials have entered into our sight [5].

So far, magnetic mesoporous carbon (MMC) materials have been synthesized by various methods, such as polymerization, hard template approach, and sol-gel process [6–8]. Among these, templating is the method widely used to design and fabricate porous carbon materials [9–11]. It involves infiltration of the pores of the template with appropriate carbon precursor, carbonization, and subsequent template removal. Great progress in fabrication of MMC has been made by developing various templates, such as zeolites and silica [11,2,12]. But it usually takes a long time to synthesize and requires strong corrosive acid or concentrated alkali to dissolve these templates. Moreover, the pore size of these templates is generally less than 2.5 nm [13,14], which provides a considerable diffusion barrier for carbon precursor molecules' spread. Layered double hydroxide (LDH) with large surface area, low cost, three-dimensional structure has been demonstrated huge potential for drug delivery, catalysis, sensing, and pollutants adsorption [15–19]. The orientation and dimensionality hierarchical structure as well as the large expandable interlayer free space make it easier for further modification. Specially, previous researches have reported that the LDH template could be synthesized in a short time [19] and be dissolved under mild acid pH [20], which enable it to be an ideal template candidate. Up to now, the synthesis of MMC by using LDH as template has not been reported yet.

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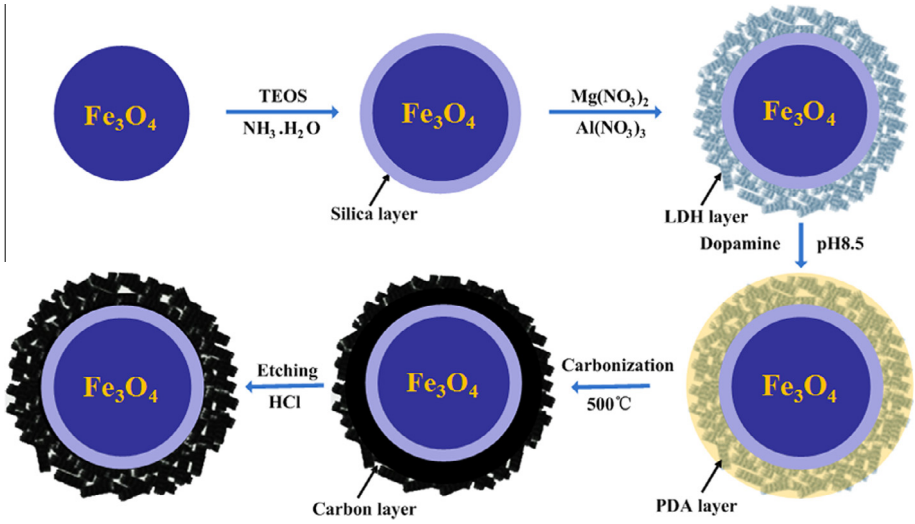

Scheme 1. Synthesis of Fe_3O_4@SiO_2@meso C (MMC) microsphere.

Glucose [21], pyrroles [22] and phenolic resins [23] are often served as carbon precursor. The hydrolysis process of these carbon precursors generally suffers from either a relatively high temperature or a water bath heating. In addition, some of precursors, such as formaldehyde and resorcinol, are harmful to people [24,25]. Dopamine, a biomolecule which contains numerous amine and catechol functional groups, has the ability of adhering to almost all material surfaces and autopolymerization to form polydopamine (PDA) coating under alkaline condition at room temperature [26]. The formation of PDA coating is simple, inexpensive and high yield and the thickness of PDA coating can be readily controlled by changing the experimental parameters. Although dopamine has been previously utilized for the surface modification of various nanoparticles [27–29], there is only limited research on preparing Fe_3O_4-based porous carbon materials by using a dopamine polymer as the carbon precursor.

Herein, we report a novel and gentle approach to synthesize flowerlike MMC microspheres by using silica coated magnetite Fe_3O_4 as core, porous Mg–Al LDH as template and dopamine as carbon precursor. Scheme 1 illustrates the synthesis of MMC materials. First, uniform magnetite nanoparticles were coated with a thin silica layer by sol–gel approach to obtain Fe_3O_4@SiO_2 composites. Then, Mg–Al LDH nanoflakes were perpendicularly deposited on the Fe_3O_4@SiO_2 microspheres (Fe_3O_4@SiO_2@LDH). Third, the free space of LDH was charged of PDA (Fe_3O_4@SiO_2@LDH@PDA) and carbonized at 500 °C. Finally, LDH templates were removed by treating with HCl to form a mesoporous carbon shell, resulting in well-dispersed Fe_3O_4@SiO_2@meso C (MMC). Compared with other methods of Fe_3O_4-based mesoporous carbon formation, additional toxic reagent and water bath are not needed. At the same time, the hierarchical porous structures of LDH template are beneficial for carbon precursor to transport and diffuse. The MMC were applied as adsorbent for the removal of 2,4,6-trichlorophenol (TCP) which has been regarded to be carcinogenic, teratogenic and mutagenic [30]. To the best of our knowledge, there has been no report on MMC prepared by LDH template with the oxidative self-polymerization of dopamine and used in the adsorption of TCP.

2. Experimental section

2.1. Chemicals and materials

All reagents were of analytical reagent grade and used without further purification. Ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), ethylene glycol (EG), magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$), aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), sodium acetate (NaAc), ammonia ($NH_3{\cdot}H_2O$), trisodiumcitrate dehydrate, 2-amino-2-hydroxymethylpropane-1,3-diol (Tris), hydrochloric acid (HCl), tetraethyl orthosilicate (Si(OC2H5)4), and ethanol (C2H5OH) were purchased from Sinopharm Chemistry Reagent Co., Ltd. (Beijing, China). 3-Hydroxytyramine hydrochloride (dopamine), and 2,4,6-trichlorophenol were obtained from J&K Chemical Ltd. (Beijing, China). A stock solution of TCP (200 mg L^{-1}) was prepared and further diluted to the desired concentrations before use. Ultrapure water used in all of the experiments was prepared by using Milli-Q SP reagent water system (Millipore, Bedford, MA, USA).

2.1.1. Synthesis of Fe_3O_4@SiO_2 nanoparticles

The Fe_3O_4 particles were prepared via a solvothermal method as described previously [29]. Then the Fe_3O_4@SiO_2 microspheres were prepared through a versatile sol–gel method [14]. In brief, magnetite Fe_3O_4 (0.85 g) was dispersed in a round-bottom flask charged with ethanol (200 mL), water (50 mL) and concentrated ammonia solution (3.60 mL, 28 wt%). The suspension was ultrasonicated for 30 min (ultrasonic cleaner, KQ-500DE, 500 W, 40 kHz). After that, 2.5 mL of tetraethyl orthosilicate (TEOS) was added dropwise followed by continuous mechanical stirring for 8 h. The resultant Fe_3O_4@SiO_2 microsphere was collected from the reaction mixture under an external magnetic field, washed with ethanol several times, and dried at 50 °C under vacuum.

2.1.2. Synthesis of Fe_3O_4@SiO_2@Mg–Al LDH microspheres

0.1 g Fe_3O_4@SiO_2 spheres were dispersed in 50 mL of deionized (DI) water (pH = 10). Then 20 mL of aqueous solution containing 1.44 mmol of $Mg(NO_3)_2{\cdot}6H_2O$ and 0.48 mmol of $Al(NO_3)_3{\cdot}9H_2O$ was dropped into the above suspension under vigorous stirring and the solution pH maintained at pH 10. After that, the mixture was under ultrasonication for 1 h (ultrasonic cleaner, KQ-500DE, 500 W, 40 kHz). The obtained Fe_3O_4@SiO_2@Mg–Al LDH microspheres were washed with DI water several times, and dried at 50 °C under vacuum.

2.1.3. Synthesis of Fe_3O_4@SiO_2@meso C composites

0.2 g of the obtained Fe_3O_4@SiO_2@Mg–Al LDH microspheres and 0.2 g of dopamine were dispersed in 100 mL of HCl–Tris solution (pH 8.5, 10 mM Tris), followed by vigorous stirring for 12 h. The precipitated black solid product (Fe_3O_4@SiO_2@LDH@PDA) was