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Hierarchical co-assembly avenue to uniform rhombododecahedral magnetic mesoporous graphitic composites

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ABSTRACT

Magnetic nanoparticles have been widely investigated due to their environmental and biomedical applications. However, the unavoidable problems associated with them are their intrinsic instability and the trend of the agglomeration. Mesoporous carbon is considered as an ideal matrix for the protection of magnetic nanoparticles owing to its high surface area, excellent chemical and thermal stability. The preparation of morphology defined composites of magnetic nanoparticles and mesoporous carbon is of great importance for their practical applications. In this work, magnetic mesoporous graphitic composites (MMGCs) with defined rhombododecahedral morphology are fabricated by the pyrolysis of the composites from the hierarchical co-assembly of amphiphilic triblock copolymer, resol oligomers and Fe_3O_4 nanoparticles. MMGCs exhibit narrow bimodal pore size distribution, high surface area and highly stable magnetic properties, which provide them excellent adsorption ability for the removal of organic contaminants in aqueous solution.

1. Introduction

Over the past decade, magnetic nanoparticles have been intensively studied for their applications in environmental treatment, information storage, bio-molecule recognition and drug delivery [1–4]. However, the unavoidable problems associated with these weakly surface-protected nanoparticles are their intrinsic instability in surrounding situation and the trend of the agglomeration. Therefore, the fabrication of morphology defined composites by burying magnetic nanoparticles in a matrix holds the key in linking their novel properties to practical applications, because such strategy not only offers protection to magnetic nanoparticles but also increases their processability. Mesoporous carbon is generally considered as an ideal matrix for such composites owing to its outstanding features including high surface area, excellent chemical and thermal stability. Until now, there are generally three strategies to synthesize magnetic nanoparticles/mesoporous carbon composites. One of them is the nanocasting strategy by the infiltration of an appropriate carbon precursor and a metal source into a mesoporous silica template, followed by thermal polymerization, carbonization and the removal of the silica framework [5–10]. In the other route, magnetic nanoparticles can be selectively supported on the pores of pre-synthesized mesoporous carbon [11,12]. Besides the above two types of multi-step synthesis approaches, a direct synthesis of magnetic nanoparticles/mesoporous carbon composites has been recently developed by using resols as carbon precursors, metal salts as magnetic components and block copolymers as the surfactant via a solvent-evaporation-induced self-assembly (EISA) approach [13–19]. However, the focus of previous work is the ordered mesostructures of the pores and the distribution of magnetic nanoparticles in mesoporous carbon matrix. The preparation of morphology defined magnetic nanoparticles/mesoporous carbon composites with controllable sizes and shapes, which is of great importance for the further patterning and integration of these composites into devices [20–26], has been rarely addressed so far.

Hierarchical assembly, which refers to the integration of self-organized nano-objects into more complex secondary structures, is one of the most promising approaches towards materials with designed morphologies and unique functions [27,28]. Nature has provided many fascinating examples of how to achieve substances with extraordinary properties by the hierarchical co-assembly of different components [29–31]. Nevertheless, the application of this technology in material sciences is still challenging since the self-assembly of diversified building blocks including small organic molecules, polymers and inorganic particles into ordered aggregates via non-covalent interactions usually requires elegant strategies and carefully selected components [32–34]. Recently, several groups have separately reported the synthesis of surfactant/polymer composites via an organic-organic self-assembly strategy [35–44]. There are two main advantages in this method: First,

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single-crystal-like surfactant/polymer composites with uniform morphology can be obtained by the careful control of the reaction conditions [43]. Second, the internal mesoporous structure of the initial surfactant/polymer composites exhibits high tolerance over the introduction of the third component such as prehydrolyzed tetraethoxysilane [45] and metal inorganic salts [13–17,46,47]. Additionally, transition metal (oxide) nanoparticles can be used as catalysts to help the conversion of polymers into graphitic carbon [48], which will improve the stability and conductivity of the resulting composites. Inspired by these results, we envision that the formation of morphology defined mesoporous magnetic carbon composites with graphitic frameworks can be experimentally feasible by the hierarchical co-assembly of surfactant, resols and magnetic nanoparticles.

Herein, we report for the first time a hierarchical co-assembly approach toward magnetic mesoporous graphitic composites (MMGCs) with defined rhombododecahedral morphology and au niform size of ∼5 μm, in which amphiphilic triblock copolymer was used as the structuring agent, resol oligomers as carbon precursors and magnetic Fe_3O_4 nanoparticles as the functional components. Upon pyrolysis at 900 °C in Ar, the resultant MMGCs exhibit a narrow bimodal pore size distribution (2.4 and 12.0 nm) and high surface area (∼230 m^2/g). Moreover, these composites exhibited highly stable magnetic properties under strong acidic due to the protection effect of graphitic shells around Fe_3O_4 nanoparticles. Additionally, the MMGCs show excellent adsorption capacities for Rhodamine B (RhB) and the magnetically-separable properties, facilitating their application as adsorbents and catalysts with an easy separation process.

2. Experimental

2.1. Chemicals

$FeCl_2{\cdot}4H_2O$, $FeCl_3{\cdot}6H_2O$, NaOH, trisodium citrate, phenol, formalin solution (37 wt%), SnO_2 suspension (∼12 nm) and poly(propylene oxide)-block-poly(ethylene oxide)-block-poly (propylene oxide) triblock copolymer pluronic F127 (M_w = 12,600, $EO_{106}PO_{70}EO_{106}$) were purchased from Acros, Aldrich, and Fluka. All chemicals were used as received without any further purification. De-ionized water was used in all experiments.

2.2. Synthesis of superparamagnetic nanoparticles

Water soluble superparamagnetic Fe_3O_4 nanoparticles were prepared by a previous described procedure [49]. Typically, a mixture of Fe^{2+} and Fe^{3+} (the molar ratio of Fe^{2+}/Fe^{3+} == 1/2) was hydrolyzed with a 2 M NaOH solution and stirred for 1 h at room temperature under Ar. After the mixture was heated up to 90 °C for 1 h, 100 ml trisodium citrate solution (0.3 M) was added. The resultant solution was then stirred for another 30 min at 90 °C, which led to the coating of magnetite Fe_3O_4 nanoparticles with citrate ions. Subsequently, the nanoparticles were collected with the help of a strong magnet and washed three times with hot water to remove the excessive reagents. Collected nanoparticles were then dispersed in water with a concentration of 17 mg/g for further use.

2.3. Synthesis of magnetic mesoporous graphitic composites with rhombododecahedron morphology

Similar to the synthesis of ordered mesoporous FDU-16 single crystals [43], magnetic mesoporous graphitic composites with rhombododecahedron morphology were prepared with modification by introducing water-soluble Fe_3O_4 nanoparticles into organic-organic self-assembly system. Firstly, 5.0 g of F127 was dissolved in 50 ml of water. Then 5 g water-soluble magnetite nanoparticles suspension (17 mg/g) was added into the above solution and stirred for 2 h to form a black homogenous suspension. Subsequently, ∼60 ml phenol/formaldehyde resols solution as polymer precursor, which was prepared by stirring the mixture of 2.0 g phenol and 7.0 ml formaldehyde solution (37 wt%) in 50 ml 0.1 M NaOH solution at 70 °C for 30 min, was added. The resultant solution containing magnetic nanoparticles was stirred at 66 °C for 72 h and then stirred at 70 °C for additional 24 h with a rate of 300 rpm. The final product was collected by the aid of external magnet, washed with water and dried in air. The obtained khaki powder was calcined at 400 °C for 3 h in Ar flow to produce magnetic mesostructured Fe_3O_4/polymer composites with single-crystal morphology, denoted as MMPCs. After further calcination at higher temperature of 900 °C for 5 h, magnetic mesoporous graphitic composites with perfect morphology (MMGCs) were derived. To investigate the stability of the resultant magnetic composites, 100 mg of MMGCs was further treated with the mixture of EtOH and con. hydrochloric acid (1:3, v/v) at room temperature. After 3 days, it still keeps strong response to external magnet.

2.4. Characterization and Measurements

X-ray diffraction (XRD) patterns were recorded on a Bruker D4 X-ray diffractometer with Ni-filtered Cu Kα radiation (40 kV, 40 mA). SEM measurements were taken on a LEO 1530 field-emission scanning electron microscope. TEM studies were performed on an FEI Tecnai F30 ST analytical TEM at operating voltage of 100 keV. The samples were dispersed in ethanol under ultrasonication and the suspension dropped on carbon-coated copper grid by evaporation in air. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 analyzer (USA). Before measurements, the samples were degassed in a vacuum at 200 °C for at least 6 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}) using adsorption branches of the isotherms, and the total pore volume (V_t) is estimated form the adsorbed amount at a relative pressure P/P_0 of 0.995. With the aid of a commercial superconducting quantum interference device (SQUID) (Quantum Design, MPMS5XL), the magnetic properties of the resultant magnetic composites were investigated by measuring the temperature-dependent magnetization after zero-field cooling (ZFC) and field cooling (FC) procedures in an applied magnetic field of 100 KOe between 2 K and 300 K. Typical hysteresis loops have been observed at 5 and 300 K. UV/Vis spectra were recorded at room temperature on a HITACHI-3010 spectrophotometer.

2.5. Adsorption and desorption

Batch-type adsorption experiments were conducted at 25 °C in the dark to evaluate the adsorption ability of MMGCs towards organic dye removal. 100 mg of MMGCs was added into the 100 ml of aqueous solution containing Rhodamine B (10–100 mg/L), and the mixture was shaken in a thermostat bath at 130 rpm and at 25 °C. Samples were withdrawn at intervals and centrifuged at 10,000 rpm for 2 min to separate liquid phases from solids, and the Rhodamine B (RhB) concentration in the supernatants was determined using UV/Vis spectrophotometer at 664 nm. At a preset time interval, aqueous samples were taken and the equilibrium concentrations of dye (C_e) were determined. The amount of adsorption (q_e) was obtained from a mass balance. Each experiment was duplicated under identical conditions to check the reproducibility. Mostly, the experimental uncertainty was less than 3%.

The procedure for desorption of MMGCs containing RhB was carried as follows: With the mixture of ethanol and water as the elute (20 mL, 50:50, v/v), the vessel containing MMGCs and elute