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Synthesis of yolk–shell magnetic magnesium silicate with tunable yolk morphology for removal of methylene blue in water

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ABSTRACT

Yolk–shell structures have attracted intensive interest owing to their unique structure and promising applications in various fields. In this study, we report a facile, effective route to prepare tubular/spindle mesoporous yolk–shell magnetic magnesium silicate. The yolk morphology and shell thickness can be readily tunable by varying the experimental conditions. The as-synthesized products have large specific surface and unique mesoporous structure. The adsorption capacities of tubular and spindle mesoporous yolk–shell magnetic magnesium silicate for methylene blue are 188 and 141 mg/g, respectively.

1. Introduction

In the past decades, morphology, structure and size of materials were widely reported to play an important on the physical and chemical properties, giving the material tremendous promise for a wide range of applications [1]. Core–shell and hollow structures have emerged as rapidly growing research themes and have made great achievements in many important research fields [2–5]. As a special class of core–shell nanostructures, integrating of the functional core, the useful shell and the cavity in between (core@void@shell configuration) which are called yolk–shell structures, have stimulated research interest for application in various fields, such as drug delivery [6], microwave absorption [7], energy storage [8] and catalysis [9] in recent years. Various methodologies have been developed to generate yolk–shell structures, which involve template-assisted [10–13], Kirkendall effect [14], Ostwald ripening [15] and galvanic reaction [16]. However, related studies were focused on how to fabricate yolk–shell structures, while the yolk morphology and porous/thickness shell were neglected. The yolk and shell structure are important parameters that can influence the practical applications [17–22]. For example, magnesium silicate nanotubes have higher adsorption capacities for lead and cadmium ions [18]; Fe_3O_4@TiO_2 yolk–shell microspheres with controllable morphology and size can effectively increase the microwave absorption properties [22]. Thus, it is very important to fabricate yolk–shell structures with desired composition, controllable yolk morphology, and well-defined shell structure, which can greatly enhance their performance.

Among various functional materials, silicate materials are the most interesting and complicated class of minerals, which have been utilized in catalysis support, bionanocomposites, magnetic-resonance imaging, and so on [23–27]. In particular, silicate nanomaterials have been used as highly efficient adsorbents in water treatment applications [28–31]. Up to now, various nanostructures of silicate have been synthesized via different routes [32–35]. The syntheses of silicate materials with high specific surface area are even more attractive for improving adsorption capacity. Furthermore, combining silicate with magnetic particles allows efficient separation and recycling during the syntheses and application by introducing external magnetic fields. Herein, yolk–shell magnetic silicate (YSMS) with the unique property of yolk, interior space, and the functionality of shell, would provide a powerful platform for improving their performance in practical applications. To the best of our knowledge, studies on the synthesis of yolk–shell magnetic silicate with different regular morphologies yolk for organic waste adsorption have been rarely reported.

In this study, we report a facile, effective route to prepare yolk–shell magnetic silicate, which is made up of mesoporous magnesium silicate shell and different regular morphologies yolk, i.e., spindle and tube (designated as s-YSMS and t-YSMS

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respectively). The synthetic route in this work can be extended as a general strategy to fabricate YSMS with different morphologies by changing the yolk materials. The s-YSMS and t-YSMS have high specific surface area and mesoporous. When used as adsorbent, the adsorption capacities of tubular and spindle mesoporous yolk–shell magnetic magnesium silicate for methylene blue are 188 and 141 mg/g, respectively. The products have excellent performance for the removal of methylene blue due to their high specific surface area and porous structures.

2. Experimental

2.1. Chemicals and syntheses

All the reagents are analytical grade and were used as received without further purification.

2.1.1. s-YSMS

Fe_2O_3 spindles were synthesized by a solvothermal method reported previously [36]. In a typical preparation procedure, 405 mg $FeCl_3{\cdot}6H_2O$ and 5.3 mg $NaH_2PO_4{\cdot}2H_2O$ were added into 75 mL water under magnetic stirring. The obtained solution was transferred into a Teflon-lined stainless steel autoclave and sealed to heat at 105 °C. After reaction for 48 h, the autoclave was cooled down to room temperature. The monodispersed Fe_2O_3 particles were centrifuged and washed with ethanol and finally re-dispersed in ethanol for subsequent use. 5 mL of the above solution containing 15 mg of Fe_2O_3 was mixed with ethanol (95 mL), H_2O (1.6 mL), $NH_3{\cdot}H_2O$ (25%, 2.5 mL) and tetraethylorthosilicate (0.36 mL) for 6 h at room temperature. The products were centrifugally separated from the suspension and washed with water and ethanol. Fe_2O_3@SiO_2 core/shell spheres (12.5 mg), urea (30 mg) and $Mg(NO_3)_2{\cdot}6H_2O$ (41 mg) were added into the mixture of water (10 mL) and ethanol (5 mL). The suspension was transferred into a Teflon-lined stainless steel autoclave with a capacity of 25 mL, kept at 190 °C for 24 h, and then cooled to room temperature. The products were collected by centrifugation and washed with deionized water and ethanol. To prepared yolk–shell magnetic magnesium silicate, 100 mg of the spindle Fe_2O_3@magnesium silicate was placed in a quartz boat in the middle of a horizontal tube furnace, and annealed at 360 °C in flowing hydrogen/argon gas (80 mL min^{-1}/120 mL min^{-1}) for 10 h. Then the furnace was cooled down to room temperature in the flowing gas. After H_2 deoxidation, the color of the sample changed from red–yellow to black.

2.1.2. t-YSMS

The Fe_2O_3 tubes were synthesized according to a solvothermal method as described previously [37]. The t-YSMS, which was made up of mesoporous magnesium silicate shell and tubular yolk, was obtained by similar procedures except for the use of tubular Fe_2O_3 as core and H_2 deoxidation 5 h.

2.2. Characterization

The products were analyzed by powder X-ray diffraction with Cu Kα radiation (36 kV, 25 mA) from 10° to 80°. The morphologies were obtained by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM-2100). The surface area of the products was measured by Brunauer–Emmett–Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system. Pore size distribution plot was obtained by Barrett–Joyner–Halenda (BJH) method. Magnetic measurements were carried out by using physical property measurement system (PPMS, Quantum Design).

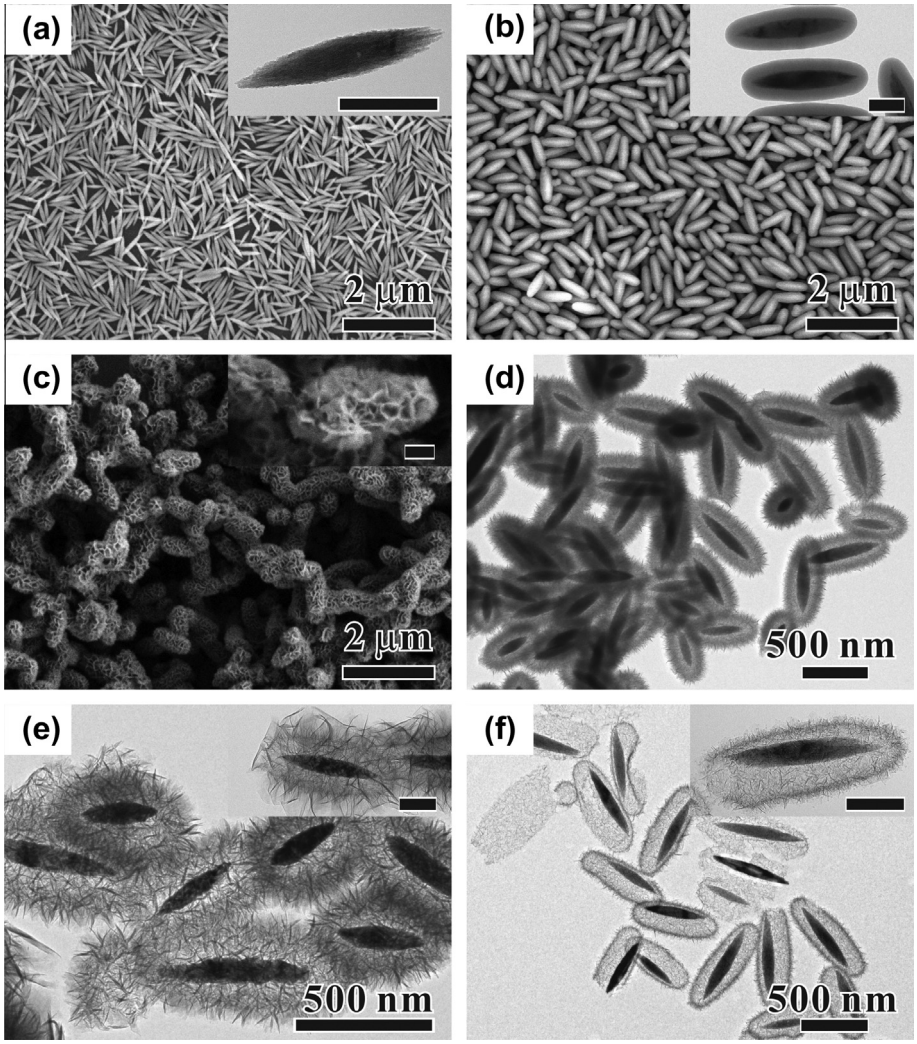

Fig. 1. (a and b) SEM and TEM images of the spindle α-Fe_2O_3 and Fe_2O_3@SiO_2, respectively; (c and d) SEM and TEM images of the spindle Fe_2O_3@magnesium silicate; (e) different magnification TEM images of the s-YSMS; (f) the s-YSMS at 0.08 mmol Mg^{2+}; all inset scale bars are 200 nm.