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Facile hard template approach for synthetic hectorite hollow microspheres

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ABSTRACT

A facile route for the synthesis of synthetic hectorite hollow microspheres (SHHMS) having a diameter of 4–6 μm and wall thickness of 30–50 nm has been demonstrated. Carbon spheres obtained from the autogenic pyrolysis of polypropylene have been utilized as a template for the synthesis of SHHMS. The formation of the hectorite architecture was confirmed by X-ray diffraction and infrared spectroscopy. The scanning and transmission electron microscopic studies reveal their spherical and hollow nature. The morphology of the obtained product was dependent on the amount of carbon spheres template. The obtained SHHMS showed the mesoporous textural property with enhanced carbon dioxide adsorption capacity (19.2 cm^3/g) as compared to that of calcined hectorite (15.3 cm^3/g) at 303 K.

1. Introduction

Since past decade, the hollow spheres structure of inorganic materials have attracted considerable attention of research community due to their low density and higher surface area compared to the bulk material [1]. These properties of hollow spheres make it a potential candidate in the field of controlled drug delivery, cosmetic, filler, catalysis and adsorption [2,3]. Different metal, metal oxides, ceramic, carbon and silicates hollow spheres have been synthesized using different methodologies due to their potential application in various fields [4,5].

Template mediated synthesis is one of the well-studied and easy methodology for the preparation of hollow structures with desired shape and size [3]. Recently we have demonstrated the use of carbon spheres as template for the synthesis of CuO hollow microspheres [6]. Synthetic clay possessing tailored pore structure, unique swelling, intercalation and ion exchange properties, is a versatile and low cost adsorbent [7–9]. The first synthesis of Laponite hollow microspheres is reported by Caruso et al. [10] using layer by layer deposition on polystyrene template. Thereafter, Bourlinos et al. [11] and Muthusamy et al. [12] synthesized clay hollow microspheres using spherical anion exchange resin and emulsion technique, respectively. The spray-drying technique is also an alternative pathway for the synthesis of clay hollow microsphere [13]. In this paper, we have demonstrated a simple and convenient route for the synthesis of synthetic hectorite hollow microspheres (SHHMS) using carbon spheres as hard template.

2. Experimental

The carbon spheres utilized as the template for SHHMS was synthesized by the reported method [6]. The synthesis of hectorite was carried out with the modification in the reported methodology [14] with reactants in the molar ratios of LiF:MgO:SiO_2=0.266:1.00:1.52. In the first step, the carbon spheres were coated with the required amount of $Mg(OH)_2$. For this, carbon spheres (0.5 g) were dipped in 10 mL of 1:9 (V/V) methanol–water mixtures and ultrasonicated for 30 min. The precipitation of magnesium hydroxide was carried out using $MgCl_2 \cdot 6H_2O$ (0.325 g) and 15 mL of ammonia solution followed by aging at 80 °C for 3 h. The obtained $Mg(OH)_2$ carbon sphere composite was centrifuged and further used for the synthesis of hectorite without drying. The synthesis of hectorite was carried out under reflux condition (120 °C for 48 h without stirring) using $Mg(OH)_2$ carbon spheres composite, distilled water (10 mL), LiF (0.0102 g) and Ludox HS-40, a Na^+-stabilized 40% silica sol (DuPont) (Sigma-Aldrich, USA) (0.37 g) as silica and sodium source. Filtration and sufficient water washing followed by drying at 100 °C for 8 h resulted into the hectorite coated carbon spheres (SH@CS).

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SHHMS was obtained by the calcination of SH@CS at 500 °C for 2 h at the heating rate of 1 °C/min. The content of carbon spheres was varied from 0.5 to 2.0 g and the obtained SHHMS was denoted as SHHMS_0.5 in which the last digits indicates the amount of carbon spheres used.

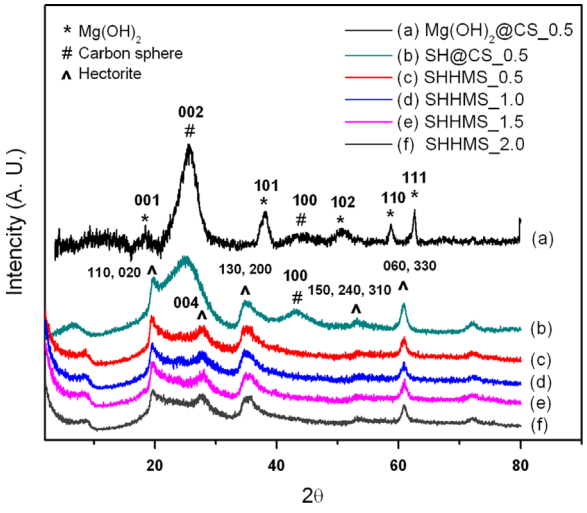

Fig. 1. XRD pattern of (a) $Mg(OH)_2$@CS_0.5, (b) SH@CS_0.5, (c) SHHMS_0.5, (d) SHHMS_1.0, (e) SHHMS_1.5 and (f) SHHMS_2.0.

3. Results and discussion

During the synthesis of SHHMS, each step of the preparation was monitored by the XRD analysis. In the first step of the synthesis, the carbon spheres were uniformly coated with magnesium hydroxide using the precipitation method. The XRD pattern of $Mg(OH)_2$@CS_0.5 (Fig. 1a) clearly shows the characteristic peaks of magnesium hydroxide at $2\theta = 19.5°$ (001), 37.9° (101), 50.5° (102), 58.6° (110) and 62.1° (111) which is also in support with the observations made by Wang et al. [15]. The broad diffraction peak observed at 2θ of 25.3° is the characteristic peak for the carbon materials due to 002 plane of graphitic arrangement [16]. The characteristic XRD pattern of the SH@CS composite (Fig. 1b) at $2\theta = 19.6°$ (110, 020), 28.3 (004), 35.1° (130, 200), 52.9° (150, 240, 310) and 61.0° (060, 330) confirmed the formation of the clay shell on the carbon sphere surface. The calcination of SH@CS composite completely removes the carbon sphere template without significantly affecting the hectorite architecture (Fig. 1c) and resulting in to the SHHMS. The chemical composition of SHHMS based on ICP analysis is 1.3% Li_2O, 2.7% Na_2O, 28.1% MgO and 63.1% SiO_2 which corresponds to the ideal hectorite composition: $Ex_{0.66}$ $[Li_{0.66}Mg_{5.34}Si_8O_{20}(OH)_4]$, where Ex = exchangeable monocation.

The hectorite product obtained using 0.5 g of carbon spheres as template shows the formation of hectorite particle with spherical cages (Fig. S1a) after calcination at 500 °C. Moreover less amount of carbon spheres used as template also resulted into the formation of hectorite particles with spherical cages (Fig. S1a). The XRD

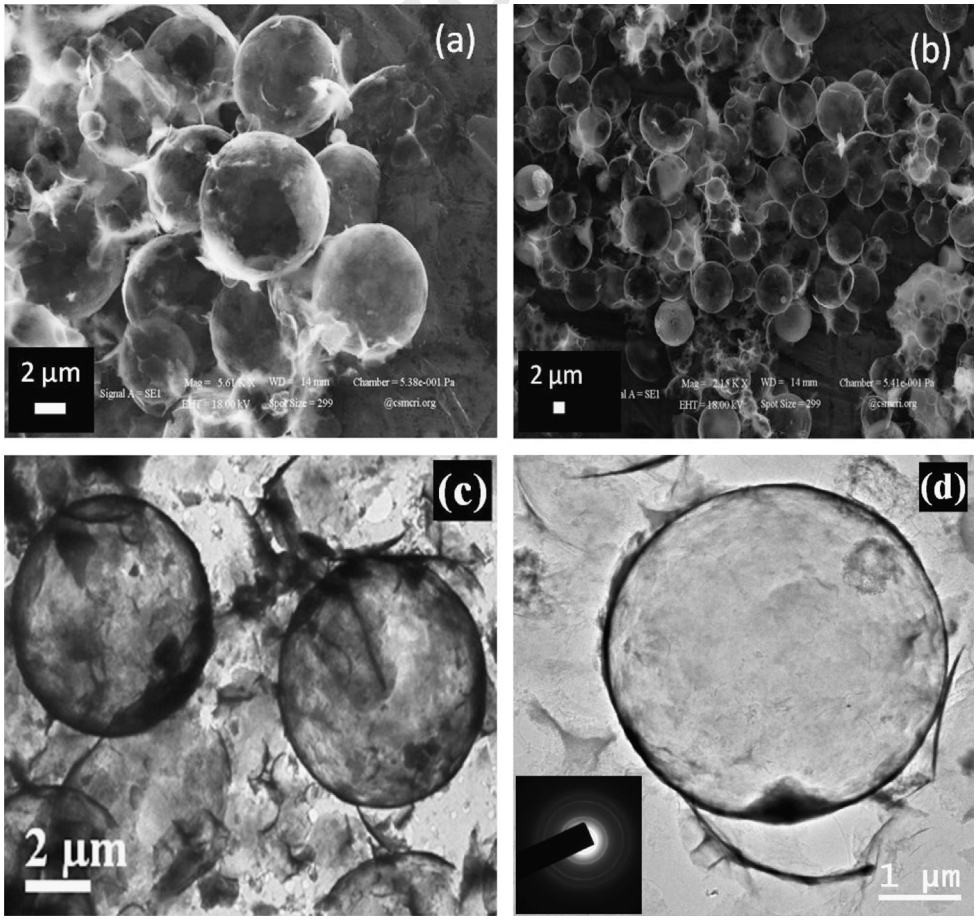

Fig. 2. SEM image of (a) SHHMS_1.5, (b) SHHMS_2.0 and TEM images (c, d) of SHHMS_2.0 showing hollow microspheres. Electron diffraction pattern of SHHMS_2.0 is shown in the inset.

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