Fabrication of hollow zeolite spheres

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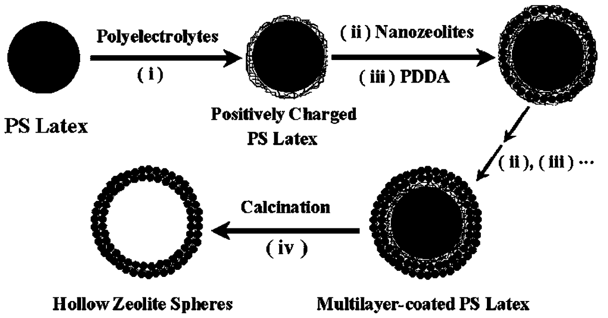
Hollow spheres of zeolite have been fabricated through a layer-by-layer technique using polystyrene spheres as templates and nanozeolites as 'building blocks', followed by calcination.

Hollow spheres have found many applications in chemistry, biotechnology and materials science owing to their characteristic macroscopic structure.[1,2] Fabrication of hollow spheres with well defined nanoscaled pores on the shell may open up possibilities for various new application fields, such as controlled release capsules, artificial cells, chemical sensors, shape-selective adsorbents and catalysts. Up to now, only hollow spheres of mesoporous silica have been obtained by spray drying and emulsion/phase separation techniques.[3–5] Zeolites are ideal construction materials for the shell of hollow spheres owing to their high thermal stability, large microporosity, high shape-selectivity and intrinsic chemical activity. However, the present methods of preparing hollow mesoporous silica spheres cannot be used to fabricate hollow zeolite spheres, because the synthetic conditions and formation mechanisms of mesoporous silica and zeolites are totally different. Recently, a layer-by-layer (LbL) technique based on electrostatic interaction or hydrogen bonding has been widely adopted to fabricate films on the surfaces of flat and spherical substrates.[6,7] It has been noticed that colloidal zeolites are negatively charged in basic solution and can aggregate readily to form hierarchical structures such as membranes, fibers and micro/macroporous zeolite monoliths.[8,9] The electrostatic attraction between a negatively charged nanozeolite and an oppositely charged polymer is an effective driving force for the self-assembly of zeolite–polymer multilayers on colloidal templates. A new procedure for fabricating hollow zeolite spheres involving polystyrene (PS) latex templated electrostatic LbL self-assembly of nanozeolite/polymer multilayers followed by removal of the template and the polymer is reported in this work.

Nanocrystals of zeolite β (40 ± 5 nm), silicalite-1 (50±10 and 80 ± 10 nm) were prepared according to the literature methods,[10,11] and characterized by XRD, IR and SEM. The nanozeolites were centrifuged, washed and dispersed in 0.1 mol L^{-1} NaCl solution at pH 9.5. The fabrication procedure for hollow zeolite spheres is depicted in Scheme 1. First, the positively charged PS latex templates were prepared by depositing five layers of polyelectrolytes of cationic poly(diallyldimethylammonium chloride) (PDDA) and anionic poly(styrenesulfonate, sodium salt) (PSS) in the order of PDDA/PSS/PDDA/PSS/PDDA.[2,7] Then, the nanozeolite and PDDA were alternately deposited on the positively charged PS substrates to form homogeneous nanozeolite/PDDA multilayers. All the above adsorption steps were performed in 0.1 mol L^{-1} NaCl solution with a liquid/solid volume ratio of 50 at pH 9.5 and ambient temperature for 20 min, and after each adsorption step the sample was centrifuged, washed and redispersed. To remove the PS latex template and the polymers, the samples were heated to 873 K at a heating rate of 5 K min^{-1} in nitrogen, and kept at 873 K in nitrogen for 4 h and subsequently in air for 8 h.



Scheme 1 The procedure for preparing hollow zeolite spheres.

Homogeneous deposition of nanozeolite particles on PS latex templates is a crucial step in the preparation of hollow zeolite spheres using the LbL technique. The success of this process largely depends on the electrostatic interaction between the nanozeolite and PDDA. Hence, pH and ionic strength of the colloidal solution are important. In neutral solution, most of the coated spheres are coalesced and have very rough surfaces [Fig. 1(a)]. In addition, the nanozeolite particles form aggregates in solution. This is probably because the charge density on the nanosilicalite-1 surface is rather low near its isoelectric point (pH = 7).[12] At pH 11, discontinuous defects [see arrows in Fig. 1(c)] on the sphere surface are observed even after four nanozeolite/PDDA layer pairs are deposited. Under such conditions, most of the silanol groups on the surface of the nanozeolite particles exist in the form of Si–O^{-}, which increases the repulsive force between the particles and inhibits the formation of a compact coat. The best result is obtained at pH 9.5 [Fig. 1(b)], when the amount of negative charge on the zeolite particles is just adequate for them to deposit onto the positively charged PS spheres densely and compactly. NaCl was added into the solution to adjust the ionic strength. Without adding salt, defects were observed on the sphere surface even after four layers of zeolites were deposited. As the salt concentration was increased to 0.1 mol L^{-1}, the coat on the sphere surface became uniform and dense. This shows that a proper ionic strength of the solution is necessary to screen the nanozeolite particles from mutual repulsion and to facilitate the formation of a uniform and compact zeolite coat on the templates.[13]

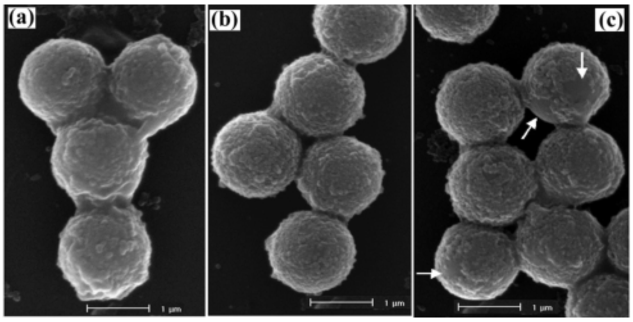


Fig. 1 SEM micrographs of polyelectrolyte-modified PS latices deposited with two nanosilicalite-1/PDDA layer pairs, (a) in neutral solution, (b) at pH = 9.5 and (c) four nanosilicalite-1/PDDA layer pairs at pH = 11.0.

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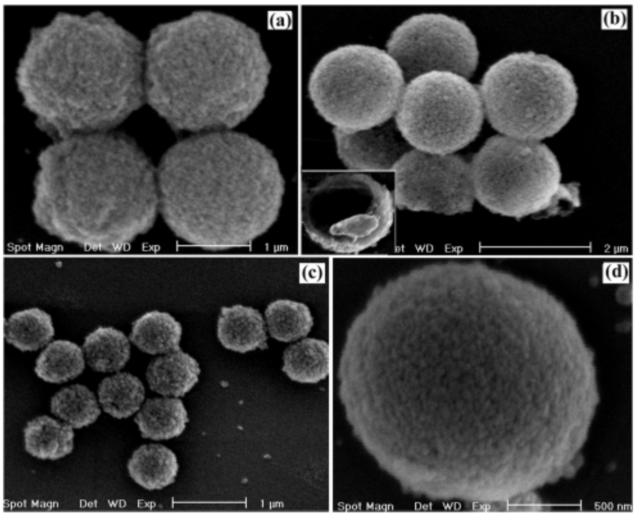

Fig. 2 SEM micrographs of samples deposited with four nanozeolite/PDDA layer pairs, (a) PS latices (ϕ = 1.47 μm) coated with zeolite β, (b) hollow zeolite β sphere templated by PS latices (ϕ = 1.47 μm), (c) hollow zeolite β sphere templated by PS latices (ϕ = 0.53 μm), (d) hollow silicalite-1 sphere templated by PS latices (ϕ = 1.47 μm).

SEM micrographs of hollow spheres of zeolite β and silicalite-1 templated by PS latices with diameters ϕ of 1.47 and 0.53 μm are shown in Fig. 2. The PS latices are homogeneously covered with zeolite nanoparticles. The inset in Fig. 2(b) shows that the spheres are hollow after calcination and the thickness of the shell is rather uniform. The surface of the hollow spheres is smoother than the coated PS latices, implying that the zeolite nanoparticles are more closely packed after calcination. Also, it was observed that the smaller the PS latices and the nanozeolite particles employed, the easier it was to keep the hollow spheres intact. Almost all the hollow spheres were intact, when the samples were prepared by depositing four layers of 40 nm zeolite β onto PS latices of 0.53 μm [Fig. 2(c)]. The percentage of intact spheres in the final product was also influenced by the number of deposited nanozeolite layers. Hollow spheres were not formed if only one layer of zeolite was deposited, but the formation of such spheres did occur, under the appropriate conditions, when two layers were deposited. The shell thickness of the hollow spheres could be tailored through varying the number of deposited nanozeolite layers. The thickness of shells composed of two, four and six layers of zeolite β nanocrystals was *ca.* 70, 140 and 200 nm, respectively.

XRD patterns of calcined hollow spheres of zeolite β and silicalite-1 are shown in Fig. 3. The patterns are almost the same as those of the original nanozeolites of zeolite β and silicalite-1, indicating that the crystalline structure and crystal size of the zeolites are unaltered after fabrication. Energy dispersive X-ray analysis established that the elemental composition of the shell is in accord with the nanozeolites used. Only characteristic bands of the zeolites appear in the IR spectra of the calcined samples,[10,11] indicating the PS latex core and other organic species are totally removed. Such novel materials are expected to have potential applications as controlled release capsules, artificial cells and catalysts owing to their unique 'cage structure' with microporous shells.

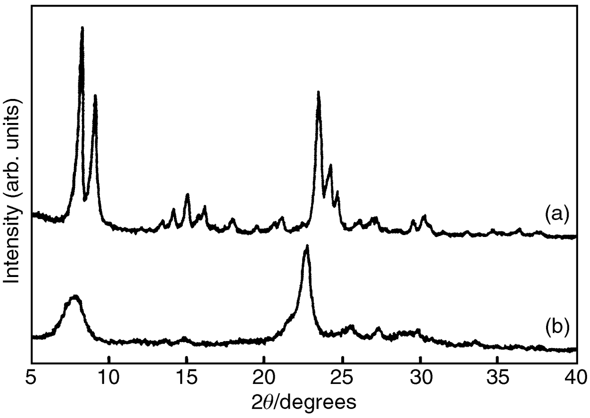

Fig. 3 XRD patterns of hollow spheres of silicalite-1 (a) and zeolite β (b).

In conclusion, hollow spheres of zeolite β and silicalite-1 with different sizes were fabricated efficiently and conveniently through LbL self-assembly of nanozeolite–polymer multilayers on a PS latex, coupled with removal of the core by calcination. The pH and ionic strength of the colloidal solution, crystal size of nanozeolites and size of PS latex templates are factors affecting the fabrication of hollow zeolite spheres. Hollow spheres of other zeolites such as ZSM-5 and TS-1 have also been successfully fabricated in the same manner (to be published). Currently, the application of these novel materials in catalysis, separation and delivery systems is in progress in our laboratory.

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