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LAYER-BY-LAYER ASSEMBLY OF NANOZEOLITE BASED ON POLYMERIC MICROSPHERE: ZEOLITE COATED SPHERE AND HOLLOW ZEOLITE SPHERE

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LAYER-BY-LAYER ASSEMBLY OF NANOZEOLITE BASED ON POLYMERIC MICROSPHERE: ZEOLITE COATED SPHERE AND HOLLOW ZEOLITE SPHERE

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ABSTRACT

Zeolite β , silicalite-1, ZSM-5, and TS-1 coated spheres have been prepared successfully through layer-by-layer assembly of nanozeolite/polymer multilayers on polystyrene (PS) microspheres, and hollow zeolite spheres have been obtained by removal of the core by calcination. In the adsorption process of nanozeolites onto the polyelectrolyte-modified template spheres, it has been found that zeta potential of the zeolite colloidal solution that determines the electrostatic interaction has important effects on the zeolite adsorption procedure. The charge on the original sphere template is not necessary, because proper polyelectrolyte modification could change the surface property of the template and make it suitable for layer-by-layer adsorption. The influences of zeolite type and/or size (40–120 nm), the number of zeolite/poly(diallyl-dimethylammonium) layer pairs, and the template sphere size (0.53–10.3 μm) on the preparation of the hollow zeolite spheres were also discussed.

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INTRODUCTION

Advanced materials fabricated by coating or templating colloidal particles often exhibit unique properties (e.g., electrical, optical, magnetic, catalytic, mechanical properties) and are therefore of extensive scientific and technological interest.^[1–6] For example, employing monodispersed colloidal spheres as building blocks, photonic bandgap crystals and three-dimensional porous materials were fabricated.^[1–4] Composite particles (or core-shell materials) produced by controlled coating of core particles with inorganic or organic layers are exploited for applications in areas of electronics, catalysis, and separations.^[5,7–9] In addition, hollow spheres obtained by removing the colloidal template also have numerous applications, including encapsulation of various products, protection of sensitive agents such as enzymes and proteins, coatings, piezoelectric transducers, and low dielectric constant materials.^[5,10,11]

A variety of procedures has been employed to manufacture core-shell particles, such as polymerization, precipitation, surface reaction, and adsorption at the surface of the core particles.^[8,12–14] Many polymer coated and inorganic coated composite particles have been fabricated by these methods, exhibiting physical and chemical properties over their single-component counterparts. In recent years, the layer-by-layer (LbL) technique based on electrostatic interaction or hydrogen bonding has been introduced by Decher et al. to fabricate composite multilayer films.^[15,16] LbL technique provides a procedure that readily allows control over the film composition, structure, and thickness. Recently, Caruso et al. have successfully extended the LbL approach on spherical particle templates to construct polyelectrolytes,^[17] inorganic nanoparticles,^[18] and proteins^[19] multilayer films.

Zeolite is one of the widely-used crystalline materials for its uniform micropores, high thermal and hydrothermal stability, high shape-selectivity, and intrinsic chemical activity. Zeolite is generally produced as particles, and further processing is required in order to tailor agglomerates to obtain useful shapes and sizes for practical application. It has been noticed that nanozeolites can aggregate readily to form hierarchical structures such as membrane, fiber, and micro/macroporous zeolite monolith,^[20,21] due to their colloidal characteristics and condensation reactions of hydroxyl groups between zeolite nanoparticles. Charged nanozeolites could be taken as “building blocks” for layer-by-layer assembly of zeolite on colloidal particles.^[22,23] Coupled with a core removal process, hollow zeolite spheres can be obtained from the precursor of zeolite-coated particles. Such hollow spheres with well-defined nano-scaled pores on the shell derived from zeolite may open up new possibilities for their applications, such as controlled release capsules, artificial cells, chemical sensors, shape-selective adsorbents, and catalysts.

In our previous preliminary work,^[22] we found that the experiment conditions, such as pH and salt concentration, should be carefully controlled in the preparation of zeolite-polymer multilayers by a layer-by-layer method. The primary motivation behind the current work was to explore the nature of these phenomena, which might also be helpful in preparing other nanoparticle-based materials with hierarchical architecture. In this paper, we will explore the function of zeta potential of the zeolite colloid in the formation of zeolite coating film on the polystyrene (PS) microsphere template and then discuss the influence of some operational parameters on the formation of the hollow zeolite spheres obtained by removing the polymer core.

EXPERIMENTAL

Materials

Poly(diallyldimethylammonium chloride) (PDDA, $M_w < 200,000$) and poly(styrene-sulfonate, sodium salt) (PSS, $M_w 70,000$) were obtained from Aldrich. Nanocrystals of zeolite β , silicalite-1, TS-1, and ZSM-5 were prepared according to the reported methods.^[24–27] The synthesis solution compositions, topology structure, and the particle size of the nanozeolites used are listed in Table 1. The negatively charged polystyrene (PS) spheres with diameters of 0.53 μm and 1.47 μm were prepared by a soap-free emulsion polymerization,^[28] and PS spheres with diameters of 2.30 μm and 10.3 μm were obtained through dispersion polymerization.^[29–31] The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system.

Table 1. The Synthesis Solution Composition, Topology Structure, and the Particle Size of Nanozeolites Used

Zeolite	Molar Composition of the Initial Synthesis Solution	Size ^c (nm)	Topology Structure ^e
Zeolite β	15 TEAOH ^a : 30 SiO ₂ : 1 Al ₂ O ₃ : 480 H ₂ O	40 \pm 5 (45 ^d)	BEA
Silicalite-1	9 TPAOH ^b : 25 SiO ₂ : 480 H ₂ O: 100 EtOH	80 \pm 10	MFI
ZSM-5	9 TPAOH ^b : 25 SiO ₂ : 0.25 Al ₂ O ₃ : 480 H ₂ O: 100 EtOH	90 \pm 10	MFI
TS-1	9 TPAOH ^b : 25 SiO ₂ : 0.625 TiO ₂ : 404 H ₂ O: 100 EtOH	120 \pm 20	MFI

^aTEAOH: Tetraethylammonium hydroxide.

^bTPAOH: Tetrapropylammonium hydroxide.

^cEstimated from SEM.

^dMeasured by DLS.

^eDetermined by XRD.

Preparation of Zeolite-Coated Spheres and Hollow Zeolite Spheres

The fabrication procedure of zeolite coated spheres and hollow zeolite spheres is described here.^[22]

First, the positively charged PS sphere templates were prepared by alternately putting as-synthesized PS spheres into the solution of cationic PDDA and anionic PSS to adsorb five (or seven) layers of polyelectrolytes in the order of PDDA/PSS/PDDA/PSS/PDDA.^[18,32] The ratio of PS spheres to polyelectrolytes solution (1 mg/mL, 0.5 M NaCl) was ca. 0.009 g/mL, and the adsorption time was 20 min. After every adsorption step, the surplus polyelectrolytes were removed by repeating the centrifugation/water wash/redispersion cycle four times.

Secondly, the nanozeolite and PDDA were alternately adsorbed onto the positively charged PS sphere substrates to form homogeneous nanozeolite/PDDA multilayers by consecutively marinating the positively charged PS spheres in 4% nanozeolite colloidal solution and PDDA solution (1 mg/mL, 0.1 M NaCl) for desired cycles. The ionic strength of the solution was adjusted with sodium chloride, and the pH was adjusted by NH₄OH or HCl solution. Each adsorption process lasted for 20 min. After every adsorption step, the excess zeolites or PDDA were removed by repeating the centrifugation/water wash/redispersion cycle four times.

Finally, the hollow zeolite spheres were produced by drying the zeolite coated PS spheres on quartz slides at room temperature, and then calcining them at 873 K at a heating rate of 5 K min⁻¹ in nitrogen, and keeping at 873 K in nitrogen for 4 hours and subsequently in air for 8 hours.

Characterization

Scanning electron microscopy (SEM) was performed on a Philips XL30 instrument. X-ray power diffraction data were obtained on a Rigaku D/MAX-IIA diffractometer using Cu K α radiation at 40 KV and 20 mA. The dynamic light scattering (DLS) spectrometer was Malvern 4700 equipped with a 100 mW argon laser beam at a wavelength of 514.5 nm at 25°C. The zeta potential of the nanozeolite was determined by Coulter DELSA 440SX at 20°C. Infrared (IR) spectra were recorded on a Perkin–Elmer 983G spectrophotometer using KBr pellets.

RESULTS AND DISCUSSION

Zeolite-Coated Composite Microspheres

Nanozeolite/PDDA multilayer shells were prepared on the PS spheres precoated with a five-layer polyelectrolyte film by LbL method at proper conditions. Figure 1 shows the representative SEM photographs of the

PDDA/PSS/PDDA/PSS/PDDA modified PS spheres (Fig. 1a) and the composite microspheres coated with one (Fig. 1b) and four (Fig. 1c) silicalite-1/PDDA layer pairs. The PS spheres modified by polyelectrolytes show smooth surface (Fig. 1a) and positive charge, favoring the adsorption of the negative zeolite nanoparticle in the subsequent step.^[33] Fig. 1b manifests that the silicalite-1 nanoparticles have been adsorbed compactly onto the PS sphere surface homogeneously. The presence of silicalite-1 nanoparticles on the PS spheres both improves surface roughness (compared with the pure polyelectrolytes-modified PS spheres in Fig. 1a) and increases the diameters of the coated PS spheres (Fig. 1b, 1c).

To understand the adsorption of nanozeolite on the charged particles, zeolite β and silicalite-1 were chosen as building blocks, and the adsorption

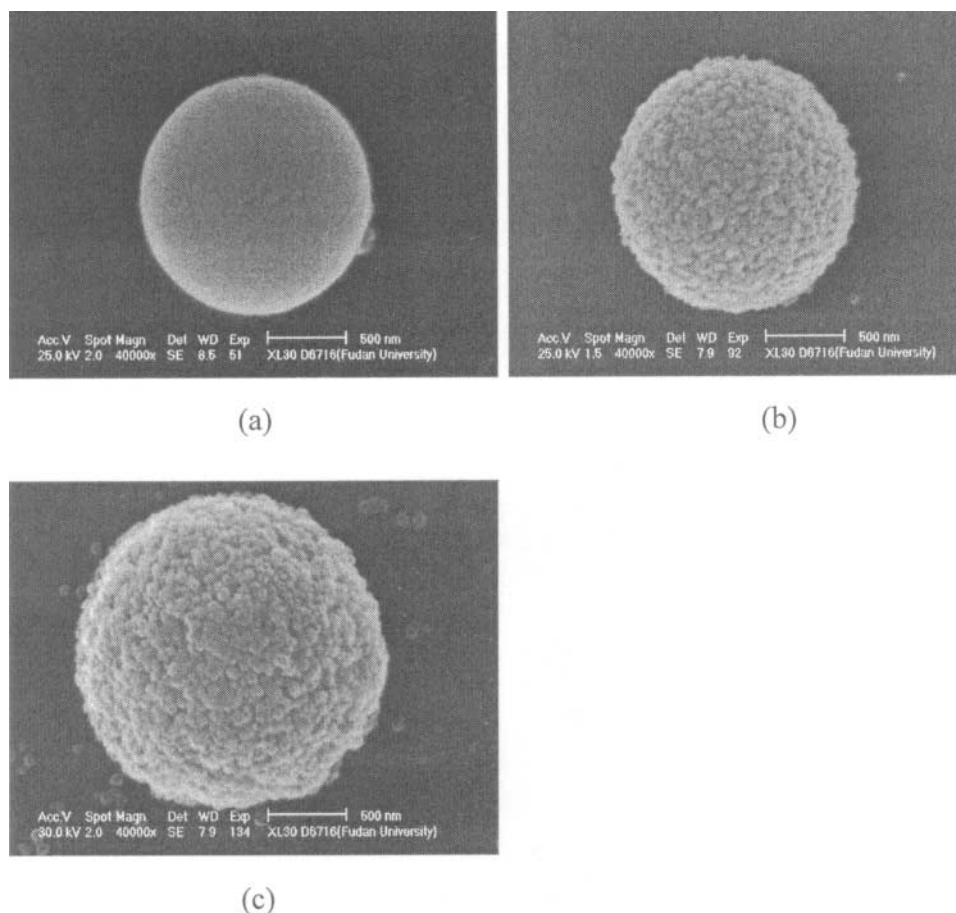


Figure 1. SEM photographs of PDDA/PSS/PDDA/PSS/PDDA modified PS sphere (a) and PS particle coated with (silicalite-1/PDDA)_N multilayer ($N = 1$ (b), and $N = 4$ (c)) at pH 9.5 and 0.1 M NaCl.

behaviors were explored under a series condition. The results are shown in Table 2, and some representative SEM photographs are presented in Fig. 2. In the situation of silicalite-1 at pH 7.0 and 0.1 M NaCl (Serial 21 in Table 2, Fig. 2a) or zeolite β at pH 3.0 and 0.1 M NaCl (Serial 32 in Table 2, Fig. 2e), the zeolite nanoparticles tend to form aggregates on the surface of PS templates and in the solution. For silicalite-1 at pH 9.5 and 0.1 M NaCl (Serial 22 in Table 2, Fig. 2b) or zeolite β at pH 7 ~ 11 and 0.1 M NaCl (Serial 33, 34, 35 in Table 2, Fig. 2f), the complete zeolite adsorption layer is obtained. For silicalite-1 at pH 9.5, the nanozeolite adsorption is loose and some interspaces (blacker area on the surface) were left on the surface of the template when ionic strength was low (Serial 24, 25 in Table 2, Fig. 2c), while a compact zeolite coating on the templates was observed for higher ionic strength (Serials 22, 23 in Table 2, Fig. 2b).

The electrostatic interaction is the basis of LbL method, and to understand the above results, the zeta potential (surface charge) of zeolite was surveyed. Due to the abundant terminal $\equiv\text{Si-OH}$ on the surface, nanozeolite could be classified as a weak electrolyte of which the zeta potential would change with pH and ionic strength.^[34] The effects of pH and ionic strength on zeta potential of zeolite β and silicalite-1 are shown in Fig. 3 and Table 2 (Serial 22–25). It is interesting that the zeta potential vs. pH curve is related to the property of zeolite framework. With the increase of pH, zeta potential of silicalite-1 with neutral framework changed dramatically from positive to negative with the isoelectric point at pH of ca. 6.7 similar to the value reported in the literature (pH ~ 7).^[35] When it came to zeolite β with framework aluminum (Si/Al = 30), the zeta-potential changed slightly and always exhibited a negative charge in the range of pH = 2 ~ 11. To inspect the effect of framework Al on the electrokinetic behavior ulteriorly, the zeta potential vs. pH curves of the zeolite β with different Si/Al ratios were also provided (Fig. 4). It was shown that the presence of more framework Al results in a shift of the IEP to lower pH.^[36] The probable explanation is that the terminal $\equiv\text{Si-OH}$ existed on the surface of nanozeolite could be protonated in acidic solution ($\equiv\text{Si-OH}_2^+$) and deprotonated in basic solution ($\equiv\text{Si-O}^-$), e.g., silicalite-1 zeolite. For zeolite β with framework Al, the bridge hydroxide groups ($\equiv\text{Si-OH-Al}\equiv$) also exist on the surface, and it can be easily deprotonated to form $\equiv\text{Si-O}^- \text{-Al}\equiv$ at a wide range of pH, making the zeolite negatively charged. For silicalite-1, only silanol group on the surface, so it has the IEP of pH 6.7. When the Si/Al ratio in zeolite β decreases, bridge hydroxide groups with negative charge on the surface will counteract the protonation of the silanol group in acidic solution, thus shifting IEP to lower pH. For zeolite β with Si/Al ratio of 30, there are abundant bridge hydroxide groups counteracting the protonation of the silanol group in acidic solution so that the zeta potential is always negative.

An increase of the ionic strength decreases the absolute value of the zeta potential of the zeolite yet does not change the characteristic with the same

Table 2. The Adsorption Behaviors of Nanozeolite on the Charged Particles

Serial No.	Nanozeolite	[NaCl]/ mol L ⁻¹	pH	Zeta Potential ^a / mV	Nature of the Template Sphere ^b	Remark ^c
21	silicalite-1	0.1	7.0	-5	+	Coalesce and aggregates
22	silicalite-1	0.1	9.5	-35	+	Dense adsorption layer
23	silicalite-1	0.01	9.5	-41	+	Dense adsorption layer
24	silicalite-1	0.001	9.5	-47	+	Loose adsorption with interspace
25	silicalite-1	0	9.5	-52	+	Loose adsorption with interspace
31	beta	0	3.0	-34	+	Dense adsorption layer
32	beta	0.1	3.0	-19	+	Coalesce and aggregates
33	beta	0.1	7.0	-30	+	Dense adsorption layer
34	beta	0.1	9.5	-37	+	Dense adsorption layer
35	beta	0.1	11.0	-35	+	Dense adsorption layer
41	silicalite-1	0.1	9.5	-35	-	Bare
42	silicalite-1	0.1	3.0	28	+	A lot of defects of vacancy
43	silicalite-1	0.1	3.0	28	-	Dense adsorption layer

^aZeta potential: The zeta potential of the nanozeolite colloid at proper pH and ionic strength.

^bNature of the template sphere: +, positive charge, the sphere coated with PDDA/PSS/PDDA/PSS/PDDA/PSS/PDDA; -, negative charge, the sphere coated with PDDA/PSS/PDDA/PSS/PDDA/PSS.

^cRemark: The adsorption phenomenon of one nanozeolite layer on the charged template sphere.

IEP (for silicalite-1), because the presence of salt decreases the range and magnitude of the repulsive double layer interaction of nanozeolites through compressing the electrical diffusion double layer.^[34,37]

From the view of the zeta potential, the rational interpretation of the adsorption behavior of nanozeolite onto a template sphere has been given. When the zeta potential of zeolites is too high, such as silicalite-1 at pH 9.5, and ionic strength is too low (Serials 24, 25), loose adsorption with inter-spaces between the nanozeolites on the surface of the template was observed, because the high density of the same charge on zeolite nanoparticles would make them repel each other in the process of adsorbing.

When the zeta potential is proper, such as zeolite β at pH 7 ~ 11 and 0.1 M NaCl (Serial 33, 34, 35), zeolite β at pH 3 and 0 M NaCl (Serial 31), or silicalite-1 at pH 9.5, and ionic strength is higher (Serial 22, 23), one complete zeolite adsorption layer is obtained. A proper increase of the ionic strength decreased the absolute value of zeta potential of the zeolite, which is neces-

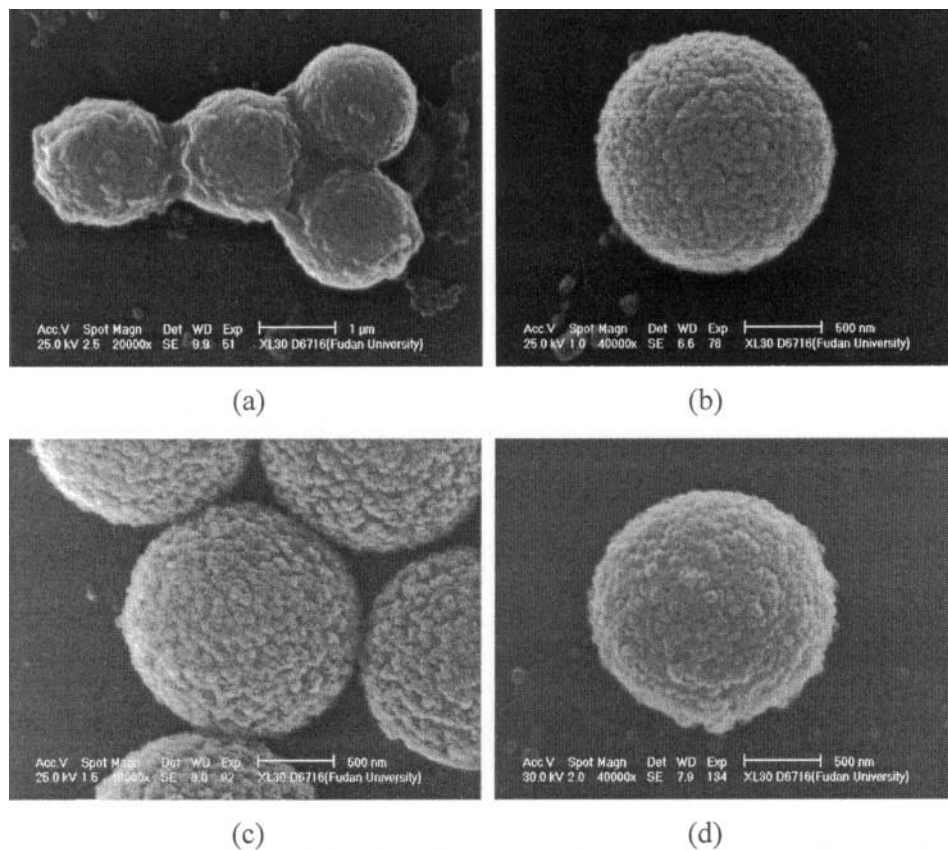


Figure 2a–d. SEM photographs of PS particle coated with (nanozeolite-polyelectrolyte)₁ layer-pair. Sample Nos. (a) 21, (b) 22, (c) 25, (d) 31.

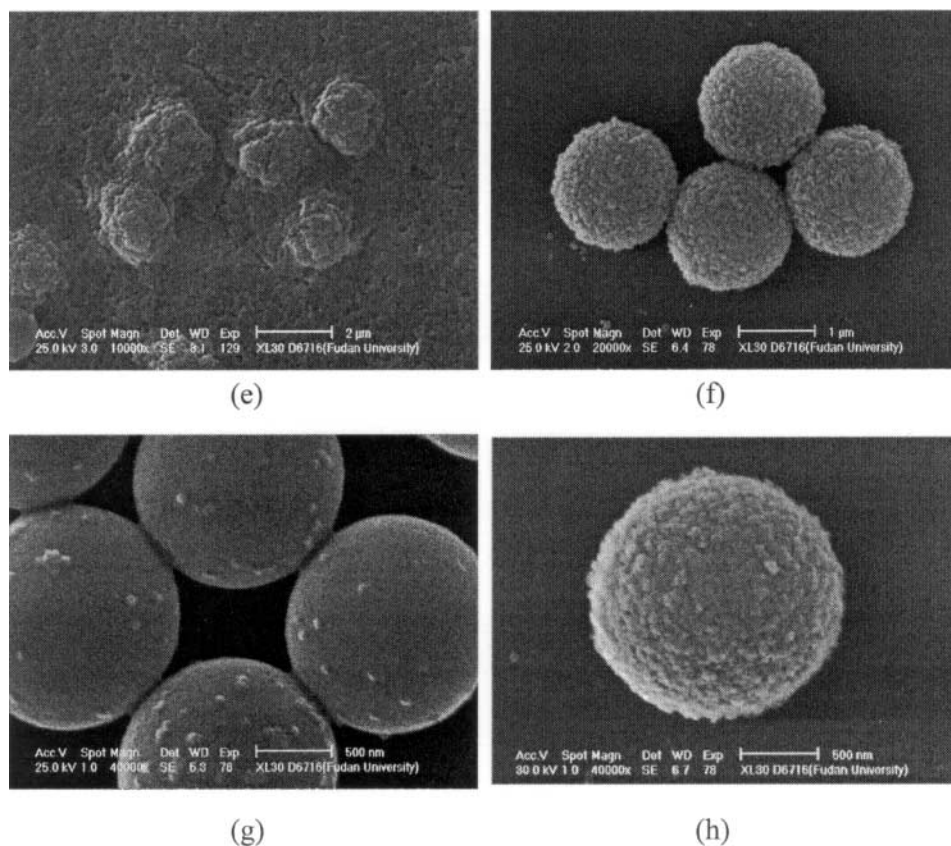


Figure 2c–h. SEM photographs of PS particle coated with (nanozeolite-polyelectrolyte)₁ layer-pair. Sample Nos. (e) 32, (f) 33, (g) 41, and (h) 43.

sary to screen the zeolite nanoparticles from mutual repulsion^[38] and to facilitate the formation of uniform and compact zeolite coating on the templates. Chen et al. also observed that the adsorption amount of SiO₂ colloids on the PDDA-modified flat substrate increased correspondingly with salt concentration until 0.2 M NaCl.^[39]

When the zeta potential of zeolite is low (such as Serial 21, 31), the surface charge density of the zeolite is not high enough, thus the zeolite nanoparticles lose stability and tend to form aggregates on the PS spheres and in the solution.

From these discussions, it can be concluded that the zeta potential of nanozeolite that determines the magnitude of electrostatic interaction has an important effect on the process of zeolite adsorption onto the template. Proper electrostatic interaction between nanozeolite and template sphere is the basis of the LbL method.^[16] When the nanozeolite is the same charge as the template sphere, few nanozeolite particles were adsorbed onto the

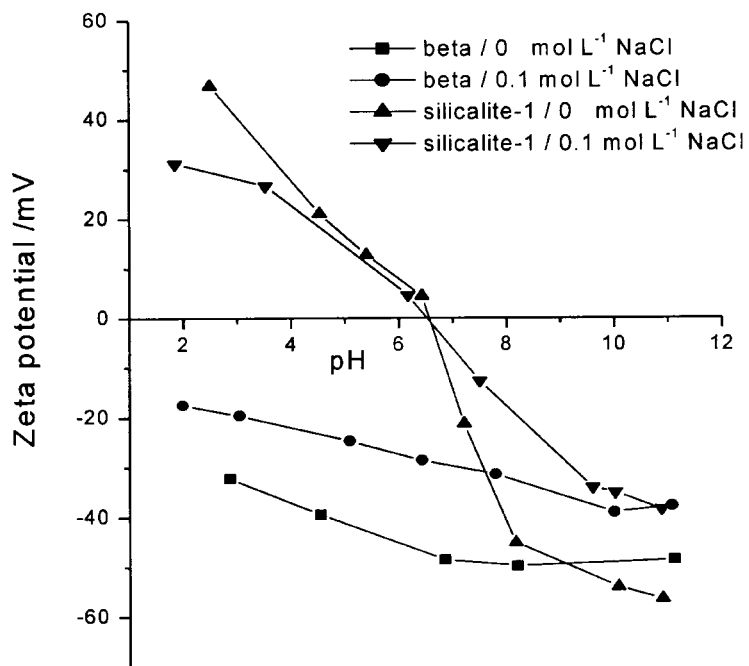


Figure 3. Effect of pH and NaCl concentration on the zeta potential of the silicalite-1 and beta zeolite at 20°C.

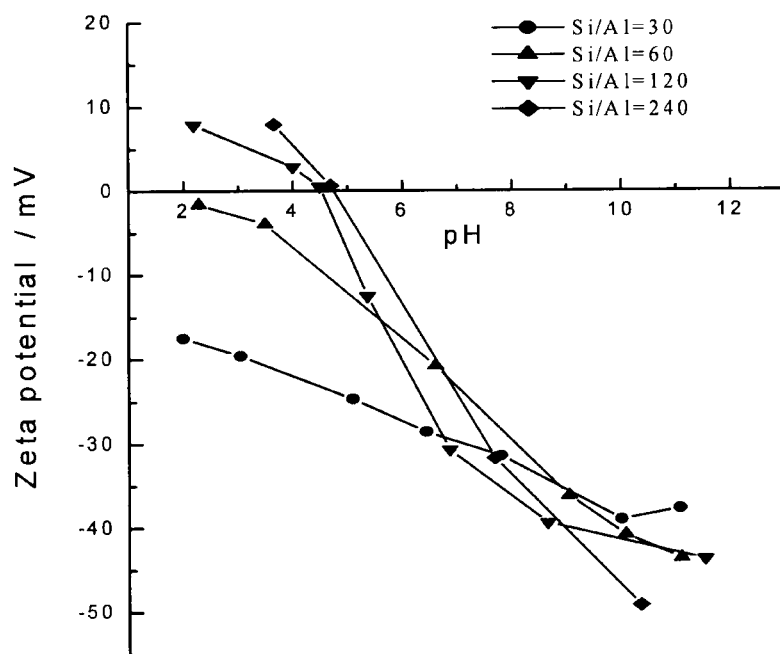


Figure 4. Effect of pH and Si/Al ratio on the zeta potential of beta zeolite at 0.1 M NaCl.

templates (Serial 41 in Table 2, Fig. 2g), or vacancy defects were observed on the surface of the templates (Serial 42 in Table 2). With the zeolite and the template sphere, one dense zeolite layer was adsorbed onto the surface of the template sphere at proper conditions (Serials 22, 43 in Table 2, Fig. 2b, 2h).

HOLLOW ZEOLITE SPHERES

Hollow zeolite spheres were obtained by calcinating the composite zeolite spheres to remove the organic template. SEM photographs show the completely hollow zeolite spheres of silicalite-1 (Fig. 5a) and zeolite β (Fig. 5b). The size match (about 80 nm) of the nanoparticles on the shell in Fig. 5a with silicalite-1 used confirmed that zeolite nanocrystals are actually “building blocks” of the shell. The inset in Fig. 5b, obtained by deliberately crushing the sample, shows that the spheres are hollow structures after calcination and the thickness of the shell is rather uniform.

The shell thickness of the hollow spheres could be tailored through varying the number of deposited nanozeolite layers. Hollow spheres were hardly formed when less than two layers of zeolite colloids were adsorbed, probably because one layer nanozeolite layer is insufficient to maintain the initial spherical structure of the PS spheres during removal of the cores.^[18] The thickness of the shell composed of two, four, six and eight layers of zeolite β nanocrystals were ~ 70 , ~ 140 , ~ 220 , and 300 nm (error in 10%), respectively.

XRD patterns of calcined hollow spheres of silicalite-1 and zeolite β (beta) shown in Fig. 6 matched well with the patterns of zeolites with MFI or BEA type structure,^[24,25] except the broadened diffraction lines as the result of small crystal size, demonstrating the nanozeolite-based characters of cal-

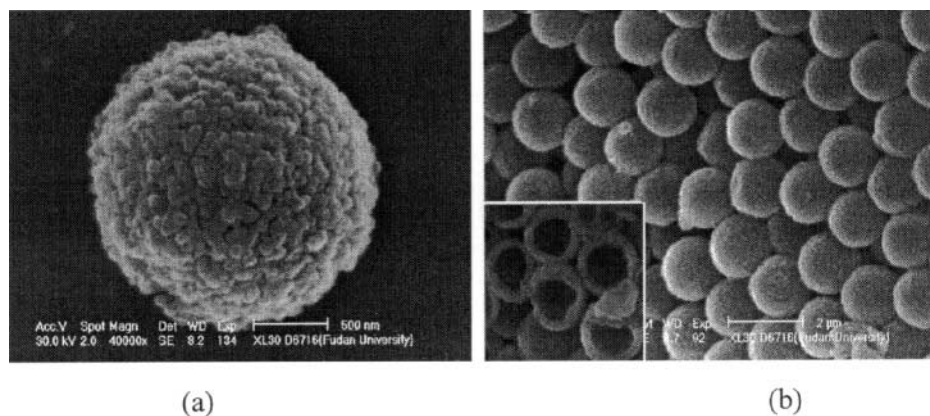


Figure 5. SEM micrographs of hollow zeolite sphere prepared by calcinating the PS latex coated with (silicalite-1/PDDA)₄ layer-pairs (a) and (β /PDDA)₆ layer-pairs (b).

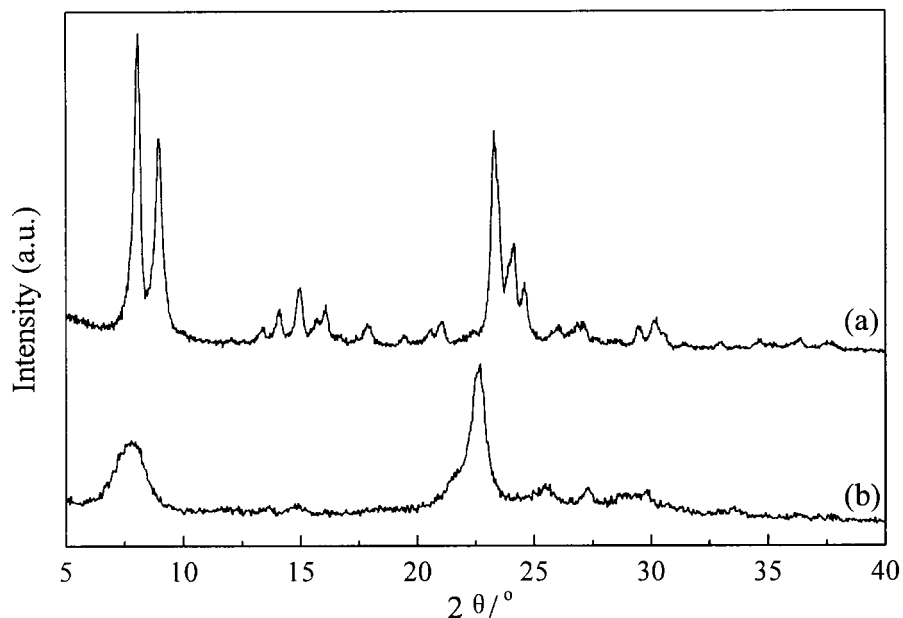


Figure 6. XRD patterns of hollow spheres of silicalite-1 (a) and zeolite β (b).

cined hollow spheres. Only characteristic bands of the zeolites appear in the IR spectra of the calcined samples (Figs. 7b and 7d) compared with composite zeolite spheres (Figs. 7a and 7c),^[24,25] indicating that the PS sphere core and other organic species are totally removed by calcination. Different from patterns of micron-sized zeolites, there is a shoulder peak at 960 cm^{-1} for the as-synthesized composite zeolite spheres, which is ascribed to silanol groups associated with the Q^3 silicon species.^[25] These bands decreased or disappeared after calcination (Fig. 7b and 7d), implying that the condensation of surface Si-OH groups on nanozeolites happened during the heat treatment process.^[21]

In order to obtain hollow spheres with cavities of different sizes, the diameters of template spheres could be tailored. Here, the PS spheres with diameters of 0.53, 1.47, 2.30, and 10.3 μm are used as templates, respectively.

PS spheres with diameters of 0.53 μm and 1.47 μm are negatively charged particles prepared by soapless emulsion polymerization.^[28] The charged spheres have been used as the templates for the LbL technique,^[17,18] and after calcining the zeolite/polymer composite sphere, complete hollow spheres have been obtained (Figs. 8a and 8b).

PS sphere templates with diameters of 2.30 μm and 10.3 μm are prepared by dispersion polymerization,^[29–31] because soapless emulsion polymerization is difficult to prepare for monodispersed spheres with diameters larger than 2 μm . However, the surface of the PS spheres obtained from dispersion polymerization bears almost no charge.^[29,30] The polyelectrolyte

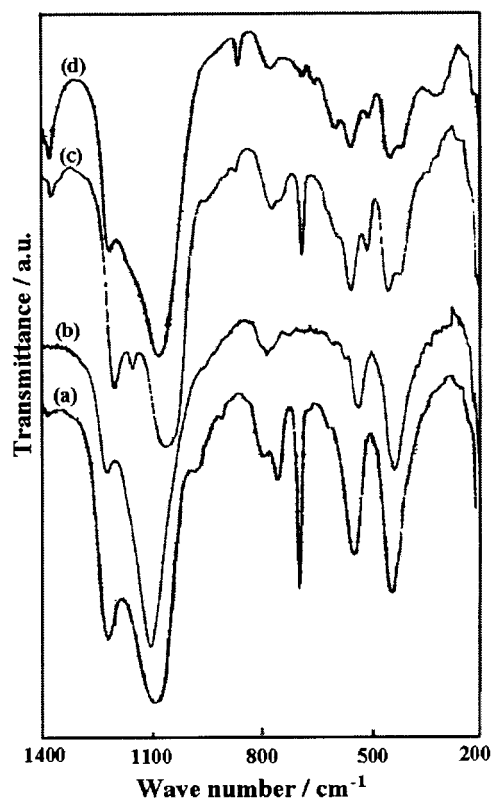


Figure 7. IR spectra of PS lattices coated with silicalite-1 (a), hollow silicalite-1 spheres (b), PS lattices coated with zeolite β (c), and hollow zeolite β spheres (d).

multilayers were also alternately adsorbed onto original uncharged PS spheres to provide enough surface charge. Maybe the interaction between the first layer of PDDA and the template PS sphere was not the electrostatic interaction but hydrophobic interaction or other interaction. After proper surface modification with polyelectrolytes, zeolite colloid had been adsorbed onto the PS sphere surface and hollow zeolite spheres also were obtained (Figs. 8c and 8d).

These results indicate that the charge on the original template is not necessary, and proper polyelectrolyte modification can change the property of the surface of the template and make it electriferous and suitable for LbL.^[40]

The zeolite nanoparticles can be observed on the sphere surface in Fig. 8a, which causes the roughness of the sphere surface. For larger spheres, although the surface seems smooth at low magnification (Fig. 8d), it is rough at high magnification (Fig. 8e), showing the existence of nanozeolite on the shell. Fig. 8f is one broken zeolite sphere of Fig. 8d, indicating the hollow structure of these spheres. In addition, it is also

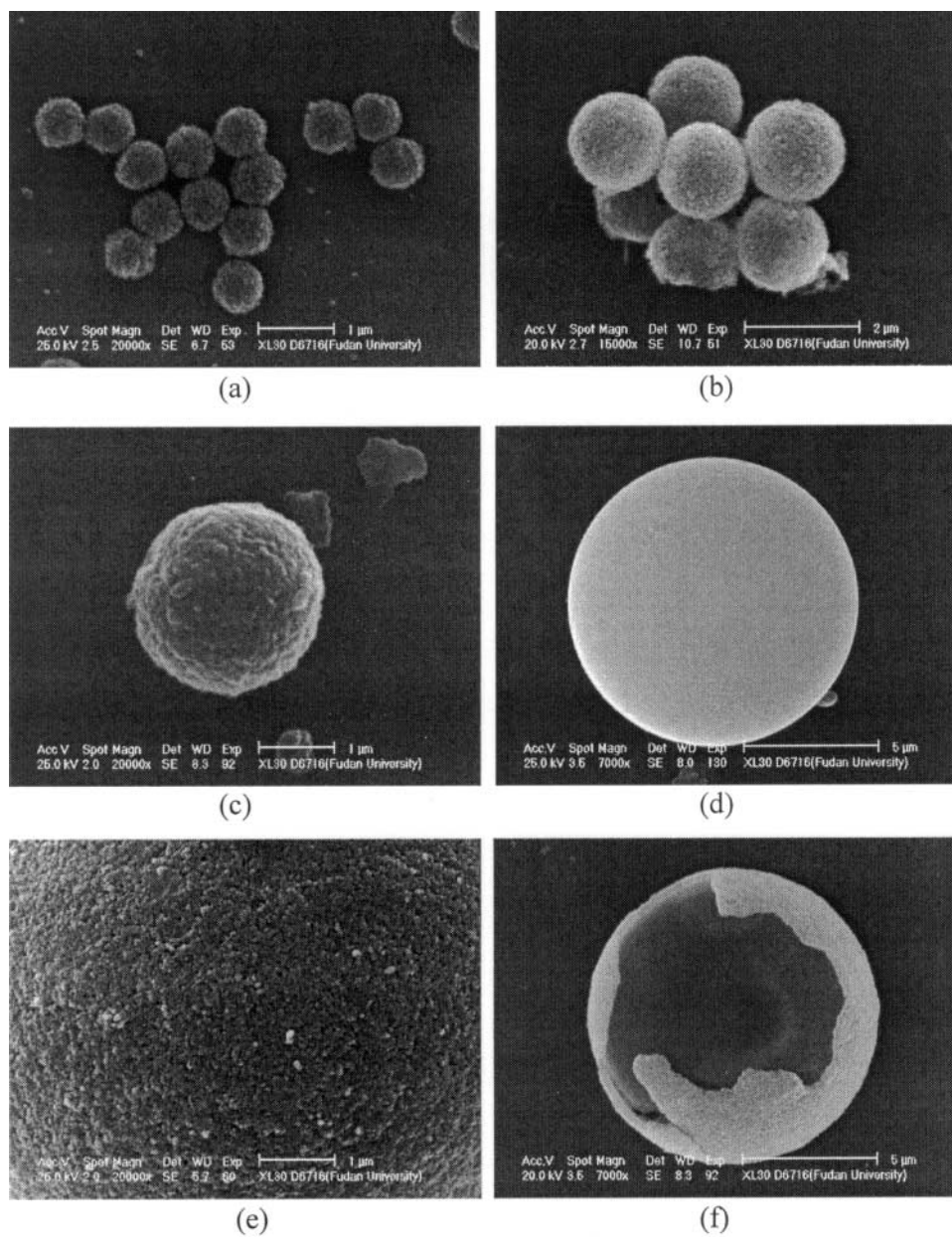


Figure 8. SEM micrographs of hollow spheres of zeolite by calcining $(\beta/\text{PDDA})_4$ layer-pairs coated PS latex with diameters of 0.53 μm (a), 1.47 μm (b), $(\beta/\text{PDDA})_5$ layer-pairs coated PS latex with diameters of 2.30 μm (c), $(\beta/\text{PDDA})_8$ layer-pairs coated PS latex with diameters of 10.3 μm (d), under high magnification (e) of sample (d), and the broken sphere (f) of sample (d).

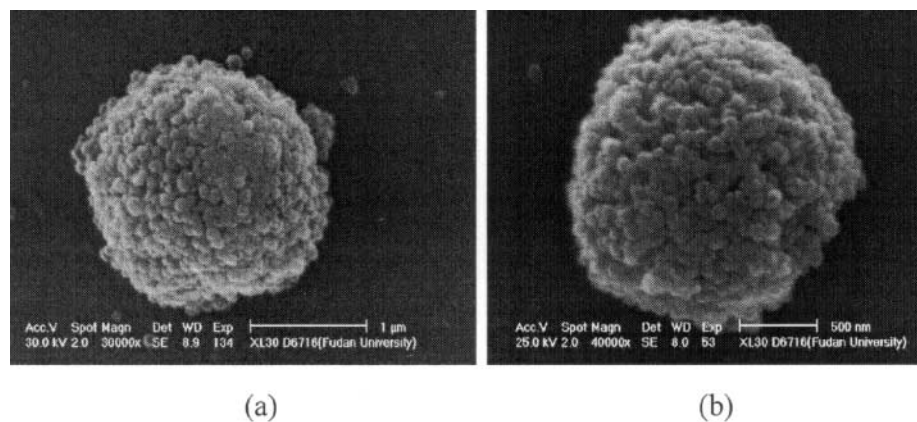


Figure 9. Hollow zeolite spheres by calcining (a) (ZSM-5/PDDA)₄ layer-pairs and (b) (TS-1/PDDA)₆ layer-pairs coated PS latex with diameters of 1.47 μm.

found that more zeolite/PDDA layer pairs might be required to obtain larger intact hollow spheres easily meanwhile keeping the original shape of the template.

Besides zeolite β and silicalite-1, hollow zeolite spheres of ZSM-5 and TS-1 were also successfully fabricated. Although the hollow sphere with ZSM-5 and TS-1 shell can be produced, it seems, by comparing Fig. 9 and Fig. 5, that the surfaces of hollow spheres prepared from the smaller zeolite nanocrystals (e.g., zeolite β with 40 nm in Fig. 5a) were smoother and more uniform than those from the larger zeolite nanoparticles (e.g., TS-1 with 120 nm in Fig. 9b). The spherical structure can also be kept perfectly intact when smaller zeolite used. It is probably because the increase of nanoparticle size results in a lower particle diffusions, a higher repulsive energy barrier, and a lower nanoparticle deposition affinity,^[38] which, therefore, prevents the formation of the more dense and complete zeolite adsorption layers. On the other hand, the increase of the zeolite nanoparticle size might also lead to the decrease of the amount of external silanols which were essential to link the zeolite nanoparticles tightly by partly fusing together during the calcination process. All above proves that the smaller zeolite nanocrystal should be the better “building block” to architect the intact spherical zeolite hollow structure by the LbL method.

Preliminary experiments have shown that the dye molecules could be diffused into the hollow zeolite spheres when such spheres were redispersed in dye solution, and the dye molecules also could be desorbed from the hollow spheres with lower velocity than adsorption. This property of the hollow zeolite spheres makes such materials suitable for drug release, and currently extensive work is taking place in our laboratory.

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