Fabrication of Hierarchically Structured Zeolites through Layer-by-Layer Assembly of Zeolite Nanocrystals on Diatom Templates

Y. J. Wang, Y. Tang,* X. D. Wang, A. G. Dong, W. Shan, and Z. Gao
Department of Chemistry, Fudan University, Shanghai 200433, P. R. China

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Zeolites with hierarchical structure were prepared through layer-by-layer electrostatic assembly of zeolite nanocrystals on the diatom substrate. The thickness and composition of the zeolite coatings on the diatom could be readily tailored by varying the number of deposition cycles and the zeolite types used, respectively.

Recently zeolites with hierarchical structure have aroused considerable research enthusiasm due to their technological promise in many important applications, such as catalysis, adsorption, separation and other advanced materials.[1–9] The previous preparation processes generally required the inclusion of removable templates on the length scale from submicron to micron, around which zeolite walls were formed using in situ zeolite crystallization,[1] seed-film method,[2] or nanozeolite self-assembly technique.[3–9] Recently, some researchers have focused on adopting stable materials with inherent hierarchical pore structure as templates, which need not to be removed to obtain macropore structure. Anderson et al.[10] have lately referred to zeolitization of diatom to acquire a hierarchically structured zeolites by a process involving ultrasonically seeding the diatoms in a silicalite-1 suspension, followed by hydrothermal growth of zeolite crystals in a reaction mixture containing adscititious tetraethyl orthosilicate. However it was difficult to control the composition and morphology of products in such process. Moreover, the overgrowth of zeolites would even stuff the internal voids of the diatom during the hydrothermal process. Recently, many endeavors have been paid to developing the layer-by-layer (LbL) zeolite assembly technique, with which it is convenient to control the zeolite film composition, structure and thickness by sequentially electrostatic deposition of charged nanozeolites and polyelectrolytes.[6–9] In this letter, the LbL zeolite assembly technique was first applied to the fabrication of zeolites with hierarchical pores using structured diatoms as templates. The advantage of this approach is that it allows readily tailoring of the composition (and consequently function) and thickness of the zeolite coatings on the diatom substrates.

Nanocrystals of silicalite-1 (80 ± 10 nm and 300 ± 50 nm), TS-1 (80 ± 10 nm), ZSM-5 (80 ± 10 nm) and beta zeolite (40 ± 5 nm) were prepared according to the literature methods[11–15] and characterized by means of XRD, IR and SEM. The initial gel composition and the isoeletric points of zeolites are listed in Table 1. The products were purified by repeated centrifugation and washing, then dispersed in distilled water to form a stable zeolite suspension with a concentration of ca. 1.0 wt% at pH 9.5 (adjusted with NH_4OH). The original diatoms (Jilin, China) consist of disc-like forms of ~ 1.2 μm in thickness and 20–40 μm in diameter with a nearly regular array of submicron pores (about 300 to 500 nm), which occupied ~ 6% volume of the raw diatom (Figure 1a). The diatoms were selected with sedimentary method in distilled water to remove the scrappy minerals.

Table 1 The composition in the gel and isoelectric point of the nanozeolites

Zeolite	Composition in gel	IEP[a]
silicalite	9 TPAOH[b]:25 SiO_2:480 H_2O:100 EtOH[c]	~6.8
ZSM-5	9 TPAOH:25 SiO_2:0.3 Al_2O_3:480 H_2O:100 EtOH	~6.0
TS-1	9 TPAOH:25 SiO_2:0.6 TiO_2:404 H_2O:100 EtOH	~6.7
beta	15 TEAOH[d]:30 SiO_2:1 Al_2O_3: 480 H_2O	<2[e]

[a] IEP: isoelectric point, measured by DELSA 440SX, Coulter. [b] PAOH: Tetrapropylammonium hydroxide. [c] EtOH: ethanol. [d] TEAOH: Tetraethylammonium hydroxide. [e] The zeta potential is negative over the entire pH range under investigation (pH=2 - 12).

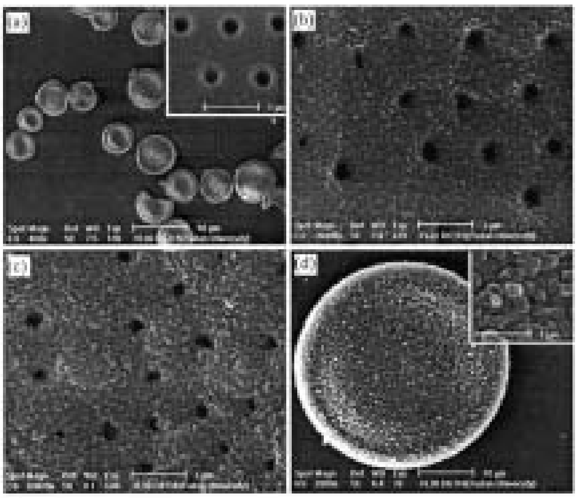

Figure 1. SEM images of the original diatoms (a), zeolite coatings on diatoms prepared with one (b) and three (c) deposition cycles using 80 nm silicalite-1 as building blocks, zeolite coatings on diatoms prepared with one deposition cycles using 300 nm silicalite-1 as building blocks (d). The insets of (a) and (d) are the magnification.

The zeolite nanocrystals were deposited onto the diatoms based on a sequential electrostatic deposition process.[7,8] First, the diatoms were positively charged by depositing a layer of cationic poly(diallyldimethylammonium chloride) (PDDA). Then, the nanozeolites and PDDA were alternately deposited on the positively charged diatom substrates to form homogeneous nanozeolite/PDDA multilayers. All the adsorption steps were done in a colloidal zeolite suspension with liquid/solid volume ratio of 50 for a duration of 15 min, followed by rinsing the samples with 0.1 mol dm^{-3} NH_4OH solution four times to remove the excess nanozeolites or PDDA. After desired layers were deposited, the samples were heated up to 823 K (heating rate 5 K min^{-1}) for 8 h in air to remove the organic species.

LbL is a very convenient way of forming mono- or multilayer nanozeolite coatings. The proper electrostatic interaction between substrates and zeolite particles is crucial to obtaining uniform and compact coatings on the diatom templates. It was found that the pH of the colloidal suspension was a fundamental factor in determining the integrity of the coatings on the diatoms. Under near neutral conditions, the charge density on the nanosilicalite-1 particles was approximately zero, thus the zeolite nanocrystals preferred to coalesce and form aggregates in the solution. With the pH value rising, the self-aggregation of zeolite particles reduced and the quality of the zeolite coatings improved due to the increase of negative zeta potential. The surface of diatoms was completely and homogeneously covered with a layer of nanozeolites after one zeolite/PDDA deposition cycle at pH about 9.5 (Figure 1b). To obtain materials with higher zeolite content, multi-step deposition process was also applied. Although the pores on the diatom plate gradually decreased as the deposition cycles increased, the hierarchical pore systems of diatoms were still kept with the diameter of macropore about 100–300 nm after three deposition cycles (Figure 1c). To further study the effect of electrostatic attraction, the pH value of the dipping solution was also adjusted below the isoelectric point (see Table 1), e.g. pH = 3.0, where the particle surface was positively charged. Only few particles were deposited on the diatoms after one nanosilicalite-1/PDDA deposition cycle since the particles were repulsed from PDDA-coated diatoms. However, when we substituted cationic PDDA by anionic polystyrenesulfonate sodium salt as poly-electrolyte, the integrated coatings on diatoms were also obtained. These results clearly show that the electrostatic attraction between the charged nanozeolite and oppositely charged polyelectrolyte is an effective driving force for the self-assembly of zeolite–polymer multilayers on the diatoms.

In the same manner, the zeolite coatings on the diatoms composed of other types of zeolite nanocrystals, such as ZSM-5, TS-1 and beta were also successfully fabricated. The larger zeolites had also been selected as building blocks to assemble on diatoms. However, with the size of zeolites increasing the surface of diatom plate was no longer compactly covered and most of the submicron pores on the plate were stuffed with zeolite crystals after one zeolite/PDDA deposition cycle (Figure 1d). A possible explanation for the comparatively loose zeolite coatings could be that the relatively weak interaction between large crystal and polyelectrolyte modified substrate and the high spatial hindrance effect of large crystal. Furthermore, hybrid nanozeolite coatings on diatom templates, which might bring about bi- and/or multi-functional materials, were also fabricated through alternately depositing different types of nanozeolites.

The XRD spectra of the samples prepared with different deposition cycles using 80 nm silicalite-1 as building blocks were shown in Figure 2. With the deposition steps increasing, the intensity of the silicalite-1 characteristic peak gradually enhanced. The IR spectra further confirmed that the composite materials comprised MFI-type zeolites. The peaks at 550 cm^{-1}, the characteristic peak of MFI-type zeolites,[11] gradually increased with the deposition cycles. From the N_2 sorption isotherms, the N_2 sorption amount of the calcined samples obviously increased after depositing nanozeolites. The micropore volume of the sample prepared using 80 nm silicalite-1 as building blocks with three deposition cycles was 0.016 cm^3 g^{-1}, while the micropore volumes of the initial diatoms and raw nanosilicalite-1 were 0.002 cm^3 g^{-1} and 0.140 cm^3 g^{-1}, respectively. The surface area rose gradually as the deposition cycles increased. For example, the surface areas of the samples prepared with one and three deposition cycles were 22 m^2 g^{-1} and 44 m^2 g^{-1}, respectively, while the initial diatoms had only the surface area of 8 m^2 g^{-1}. The fraction of zeolitic part in total weight of the prepared composite with one and three deposition cycles were ~ 10% and ~ 4%, respectively, estimated from the N_2 sorption data. If more depositing cycles were applied, the materials with higher zeolite content could also be obtained. The above results clearly indicate that the materials really comprise zeolite nanocrystals and the thickness and composition of the zeolite coatings on the diatom plates can be readily tailored by altering the deposition cycles.

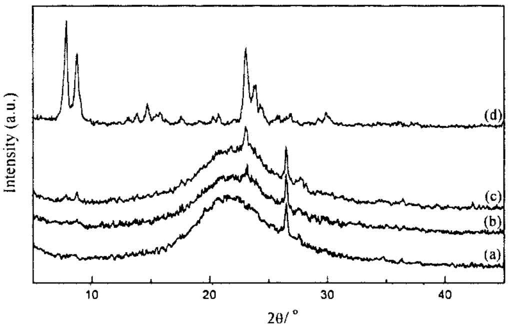

Figure 2. XRD patterns of the original diatoms (a), zeolite coatings on diatoms prepared with one (b) and three (c) deposition cycles using 80 nm silicalite-1 as building blocks, and the 80 nm silicalite-1 (d).

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