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COMMUNICATION

Hollow mesoporous zeolite microspheres: Hierarchical macro-/*meso*-/microporous structure and exceptionally enhanced adsorption properties†

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We report the synthesis of a new kind of uniform hollow zeolite microspheres with hierarchical macro-/*meso*-/microporosity by an efficient strategy combining bi-templating, steam-assisted crystallization and then a mild alkaline etching method. This novel product has a hollow architecture, highly crystallized zeolite shells and more importantly, high dye adsorption capabilities.

Hollow microspheres with various components, from carbon, metals and polymers to oxides, have drawn extensive attention for their applications in catalysis, microreactors and biomedicines, *etc.*[1–3] Among them, hollow silica mesoporous microspheres (HMS), commonly with mesoporous shells, are greatly favored, due to their advantages in mass diffusion and transport by making use of their large cavity volumes and mesopore channels on the shells.[3] However, in most available reports, the silica or silicate shells are amorphous which may limit further applications in severe circumstance.

Zeolites are a series of crystalline aluminosilicates which have been widely used as catalysts and adsorbents in oil refining, separation and environmental fields, *etc.*, due to their unique architecture, high hydrothermal stability and sufficient numbers of catalytically active sites.[4] In recent years, there has been increasing interest in developing hollow structured zeolites (HSZs), such as hollow zeolite boxes and spheres.[5–10] Since a layer-by-layer (LbL) technique based on electrostatic interaction or hydrogen bonding was reported by Caruso,[5] there have been several reports on the syntheses of HSZs using hard templates, applying LbL and/or secondary growth synthesis approaches. Valtchev *et al.* introduced a combination of LbL and hydrothermal synthesis techniques to prepare HSZs.[6] Tang *et al.* reported the fabrication of a series of HSZs using silica microspheres as hard templates and nanozeolites as building blocks, followed by hydrothermal or vapor-phase treatment.[7] In these ways, the shells are built of well-intergrown crystals so as to improve the mechanical strength of the obtained HSZs. More recently, two unique techniques for HSZs preparation involving an *in situ* transformation of silica spheres into ZSM-5 zeolite[11] under the assistance of SDA and using oil/water emulsions as templates have been reported, respectively. However, most of the above-mentioned methods were subject to the use of pre-fabricated building units such as nanozeolites. Therefore the morphology and size of HSZs are highly dependent on the hard template and the subsequent LbL technique, which further involved complicated multistep and time-consuming coating processes. More importantly, very few reports can be found focusing on HSZs with mesopores on the shells which, however, are greatly favoured due to their advantages in mass diffusion and the utilization of cavity volumes.[9]

Herein, hollow mesoporous zeolite microspheres (HMZS) with secondary mesopores on the shells were synthesized by an efficient post steam-assisted crystallization and mild alkaline etching approach (SAC-MAE). Herein, SAC and MAE have been demonstrated as effective routes to synthesize mesoporous zeolite structure (MZS) and hollow zeolite boxes, respectively, by us and other groups.[10,12] This novel product possesses uniform size of *ca.* 700 nm, hollow architecture, highly crystallized zeolite shells with mesoporous structure, relatively low diameter-to-wall ratio, and moreover, exceptionally high dye adsorption capabilities.

The fabrication strategy of HMZS involves two key steps: first, the *meso*-/micropore-structured zeolites with spherical morphology[12,13] were synthesized under steaming; and subsequently, hollow core was created by selective mild desilication in the inner part of the spheres with aqueous Na_2CO_3 solution, which finally leads to hollow mesoporous zeolite microspheres with uniform hollow architecture and unique mesoporous zeolite shells.

Mild alkaline treatment can selectively etch away the core part of a core/shell structure providing the core is structurally less compact.[9,10] We adopted this method to create hollow structure in the present case and found that the core part of MZS can be easily removed leading to the hollow structure. The SEM images of HMZS are shown in Fig. 1, which clearly demonstrate the spherical profile with size of *ca.* 700 nm. Especially, two broken particles in the centre of Fig. 1a, which were purposely selected to reveal the inner structure of HMZS, indicate the

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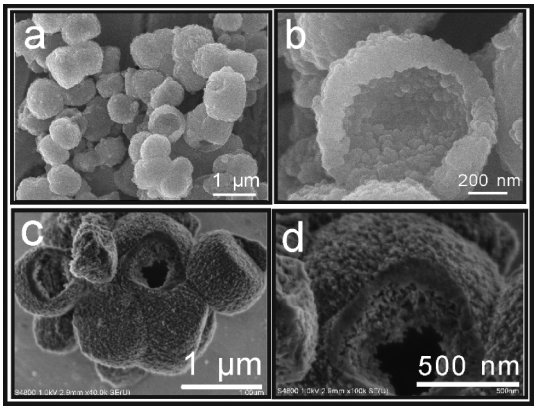

Fig. 1 SEM images of HMZS of different magnifications: (a, b) and (c, d) are the images with and without sputtering conductive layers, respectively.

hollow architecture. A higher resolution image shown in Fig. 1b further indicates that both of the internal and external surfaces are unsmooth which is characteristic of products experiencing the alkaline treatment.[9,10,14] However, more detailed feature of the HMZS surface have been covered by the conductive layer sputtered in SEM sampling for better conductivity in imaging.[15] To get more surface information, SEM images of the same sample without sputtering the conductive layer were obtained, as shown in Fig. 1c and 1d. The shell of HMZS is actually porous which is also seen in mesoporous zeolite synthesized with organosilane templating.[16] The image of higher resolution (Fig. 1d) shows that the shell possesses sponge-like structure with abundant secondary mesopores, rather than composed of aggregates of zeolite nanocrystals. Moreover, most of particles kept the spherical morphology after MAE (Fig. S2, S3, ESI†) at lower magnification and subsequently, high mechanical strength is expected for HMZS due to its unique and intact framework.

The hollow structure of HMZS was further confirmed by TEM imaging which is shown in Fig. 2. It can be found that almost all particles in the figure are spherical or near-spherical, uniform in size and hollow-structured. An accurate measurement to the size and shell thickness of HMZS indicates that the diameters of the hollow spheres are mostly in between 600 and 700 nm (650 ± 50 nm) with an average shell thickness of *ca.* 120 nm (120 ± 10 nm). So, the diameter-to-wall ratio can be calculated to be *ca.* 7/1, much higher as compared to 15/1 or larger ratios for HSZ synthesized by a LbL technique. It has been reported that a decreased diameter-to-wall ratio is a key factor in enhancing the mechanical strength.[5,6] Herein, to roughly examine the mechanical strength of HMZS, an ultrasonic treatment was performed and no cracking or damage of the spheres can be found after the treatment (Fig. S4, ESI†). The HR-TEM image of the rim part of Fig. 2c, as indicated with a square, is shown in Fig. 2e. The lattice planes of (020), (011) and (0$\bar{1}$1), *etc.*, marked in the electron diffraction pattern, could be well-ascribed to the crystal structure of ZSM-5. The single crystalline pattern and visible continuous lattice fringes indicate that the framework of the shell can be regarded as a single crystal with penetrating mesoporous network inside. In addition, thanks to the hollow structure, both the *meso*- and micro- structures can be clearly imaged on the part of the spheres (Fig. 2d, e).

It is well known that an Al distribution gradient exists in zeolite crystals. It has been known that the exterior of the ZSM-5 crystals

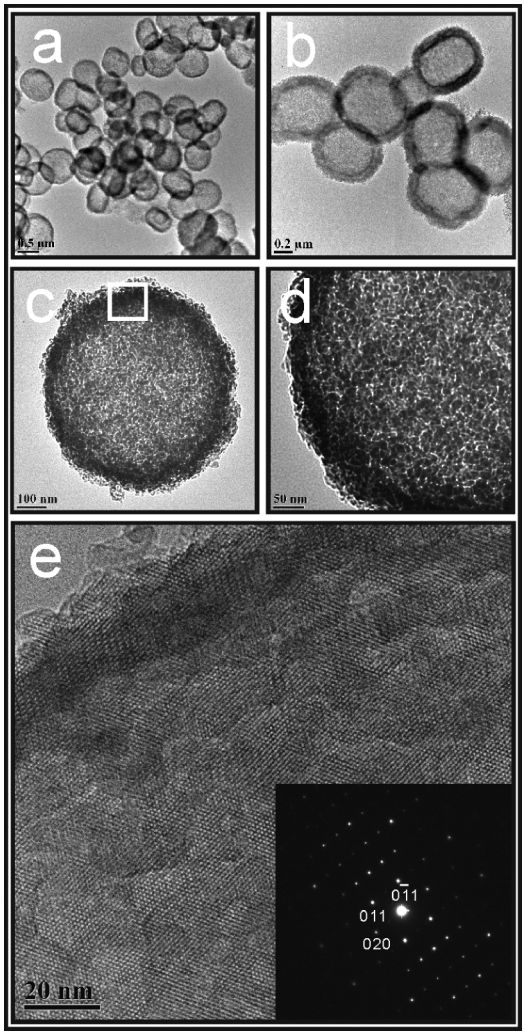

Fig. 2 TEM images (a, b and c) of HMZS at different magnifications; (d): a higher resolution image of the particle in (c); (e): HR-TEM image taken from the square frame in Fig. 2(c), and the inset in (e) is its electron diffraction pattern.

is rich in Al while the interior is poor in Al, and the negative charge associated with AlO^{4-} tetrahedrals in the zeolite framework will hinder the extraction of Al through the hydrolysis of Si–O–Al bonds by negatively charged hydroxyl groups.[17,18] Therefore, the outer shell of the zeolite is more inert to alkaline desilication than the interior due to the stabilization effect of the exterior Si atoms by nearby AlO^{4-} tetrahedrals. As a result, when subject to mild desilication (confirmed by the decrease of Si/Al ratio from 68 of MZS to 63 of HMZS in Table S1, ESI†) with aqueous Na_2CO_3 solution, the zeolite crystal (here the MZS) will undergo selective desilication from the interior, generating hollow cores in MZS and finally, porous HMZSs were obtained.

Moreover, it has been reported in literature that hollow zeolites can be created by alkaline treatment either with mild alkaline for a very long period up to 30 h (sometimes at a high temperature up to 80 °C or higher),[10] or using NaOH and/or TPAOH solution with much stronger basicity (pH > 13) in a short time (~30 min). The strong alkaline treatment would result in disorganized hierarchical architecture and in which the Si/Al ratio of zeolites are restricted in the range of 25–50.[9,14] The common point in above reports by

employing severe conditions such as long time treatment or strong alkaline circumstance is that the conventional zeolite crystals are structurally complete and intact (Fig. S4, ESI†). In contrast and interestingly, in the present case, the hollow structure is generated in a short time (no more than 3 h) in a mild alkaline solution (pH = 11.6). This can be attributed to the inherent penetrating mesoporous structure which created an easily accessible passage to its interior for the alkaline solution.

Methylene blue (MB) is commonly used as a probe molecule to determine the dye adsorption properties of as-prepared zeolite microspheres. Fig. 3 displays the adsorption isotherms and dynamic curves of MB by HMZS, MZS and ZSM-5. The saturated adsorption amount of HMZS reaches as high as 101.4 mg g^{-1}, which is almost 6 and 5 times larger than those of ZSM-5 (17.6 mg g^{-1}) and MZS (22.1 mg g^{-1}), respectively, and such an adsorption capacity is even higher than that of natural sepiolite (58 mg g^{-1})[19] and MCM-22 zeolite (60 mg g^{-1}),[20] indicating a remarkably better adsorption performance due to the large interior voids of the hollow spheres. Moreover, the adsorption dynamic curves demonstrate that almost 80% of the saturated adsorption amount can be adsorbed in less than 30 min and a saturated adsorption was achieved in 3 h for HMZS. More interestingly, HMZS is reusable and its adsorption capacity was kept as high as 54.5 mg g^{-1}, and even reused 5 times (Fig. S6, ESI†), indicating more absorption stability than amorphous hollow mesoporous spheres (HMS) which were also synthesized using the MAE method. The above results indicate a great potential for the application of as-prepared HMZS for dye removal in waste water treatment.

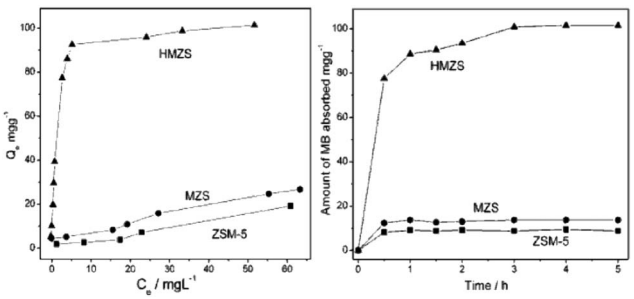

Fig. 3 Adsorption isotherms and dynamic curves of MB by (■) conventional ZSM-5 zeolite, (●) MZS and (▲) HMZS. C_e is the equilibrium concentration in the MB solution and Q_e is the amount of MB adsorbed at equilibrium concentration. The dynamic adsorptions were performed using MB solution at a concentration of 150 mg L^{-1}.

In summary, a new kind of uniform hollow mesoporous zeolite microspheres were successfully synthesized by an efficient combined strategy of a bi-templating approach and steam-assisted crystallization, followed by mild alkaline etching. This novel product possesses hollow architecture, with a submicrometer-size of *ca.* 700 nm in diameter, highly crystalline zeolite shells with penetrating mesopore structure and a low diameter-to-shell thickness ratio. More importantly, such hollow mesoporous zeolite microspheres demonstrate remarkably higher dye capabilities than conventional ZSM-5 zeolite and mesoporous zeolite spheres. More applications of HMZS in specific fields such as in heterogeneous catalysis as an efficient and sustainable catalyst, removal or separation of dyes *etc.*, are under investigation.

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