Anionic Surfactants as Nanotools for the Alignment of Non-spherical Zeolite Nanocrystals**

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One of the key elements in the success of the current worldwide emphasis on nanotechnology is the acquisition of the ability to assemble nanoparticles into highly ordered three-dimensional (3D) structures. In this regard, several methodologies have been developed, such as the slow evaporation of solvents from a nanoparticle suspension,1–9 molecular cross-linking of the functional groups tethered to the surfaces of nanoparticles,10–17 layer-by-layer assembly,18–22 and template patterning.23–26

Most of the nanoparticles that have been employed for 3D assemblies are spherical. Since spheres are symmetric in every respect, they naturally have a strong tendency to closely pack and the resulting closely packed 3D structures usually show a high ordering of the nanoscale throughout the assembled structures. However, if the morphology of the nanoparticles is non-spherical, for example cubic or octahedral, the nanoparticles are likely to orient randomly within the 3D structures, and at this stage there are no methods available to orient or align them within the 3D structures. Therefore, acquiring the ability to control the orientation or alignment of the nonspherical nanoscale building blocks within the resulting 3D structures is highly challenging and crucial for the development of nanotechnology. In conjunction with this goal, Mann and his co-workers recently demonstrated a way to assemble prismatic BaCrO₄ nanoparticles into highly ordered 1D and 2D structures through interdigitation of the surfactant molecules tethered to the nanoparticles. Despite their achievements, it is still necessary to develop methods to assemble nonspherical nanoparticles into discrete, usable, and highly ordered 3D solid objects. As a first step along the road to the final destination, we now report a novel method to align nonspherical zeolite nanocrystals at the surface of microspheres during emulsion-templated assembly of the nanocrystals into the 3D structures.

For the model nonspherical nanoscale building blocks, we employed cubic zeolite-A and octahedral zeolite-X nanocrystals (both ~150 nm). The zeolite frameworks are negatively charged because the aluminum atoms link tetrahedrally to oxygen atoms in the framework. The Si/Al ratios of the zeolites were 1.38 and 1.48, respectively. For comparison, we also prepared amorphous silica beads of diameter 200–250 nm and cylindrical zeolite-L (average length 4 μm and diameter 0.8 μm). The water droplets dispersed in toluene were employed as the templates for the assembly of zeolite nanocrystals into microspherules by modification of the method developed by Velev and Nagayama for latex spheres. The yields of microspherules are usually higher than 95%, judging from the amounts of zeolite particles in the filtered solution.

Scanning electron microscopy (SEM) analyses revealed that zeolite-A nanocrystals readily assemble into microspherules, the inset of Figure 1A shows a typical example. The diameters of the spherules usually range from 1 to 20 μm. We propose that the toluene-dispersed water droplets act as the emulsion templates to attract hydrophilic zeolite crystals into the aqueous phase, as depicted in Figure 2A. The microspherules do not disintegrate even after sonication for 10 min in water, which indicates that strong bonding develops between the zeolite nanocrystals despite the absence of any added binders. Although a systematic investigation is necessary to elucidate the exact nature of the bonding, we thereby propose that a dehydration reaction takes place between the surface hydroxyl groups of zeolite nanocrystals during sonication, which gives rise to direct siloxyl linkages between the zeolite nanocrystals. The high rigidity of the microspherules, even after calcination at 500 °C for 10 h under flowing oxygen, further indicates that they are self-supporting, and hence organic binders are not necessary for intercrystalline binding. The silica beads also form spherules by employing the same method.

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Fig. 1. SEM images of zeolite assemblies. A) A typical zeolite-A spherulite showing randomly oriented zeolite crystals at the outermost layer. Inset: the overview of spherulites. SDS = 0 mM. B) Aligned zeolite-A crystals at the outermost layer. SDS = 4 mM. C) An anisotropic 3D structure of zeolite-A crystals with high surface ordering. SDS = 20 mM. D) A typical zeolite-X spherulite with randomly oriented zeolite crystals at the outermost layer. E) The views of a zeolite-X spherulite and its surface showing highly aligned zeolite-X crystals at the outermost layer. SDS = 20 mM. F) An anisotropic zeolite-X spherulite with highly ordered outermost crystals. SDS = 50 mM.

As typically shown in Figure 3A. However, the interparticle binding force in the silica bead spherulites is much weaker than that of the zeolite spherulites, presumably due to a smaller contact area between the spherical particles.

As expected, the zeolite-A nanocrystals on the surfaces of microspherulites are randomly oriented (Fig. 1A), whereas the silica beads are highly aligned in the resulting spherulites (Fig. 3A). However, addition of an aqueous solution of sodium dodecysulfate (SDS, 4 mM) instead of pure water leads to zeolite-A spherulites with high surface ordering, as shown in Figure 1B. The SEM images of the cross sections of the microspherulites revealed that the ordering is limited to the two outermost surface layers (data available from the authors). Further increases in the concentration of SDS (> 10 mM) only leads to production of highly irregular, anisotropic spherulites, as shown in Figure 1C. However, the outermost zeolite nanoparticles of the anisotropic spherulites still remain highly ordered.

The proposed role of SDS for the above phenomena is depicted in Figure 2B. Thus, when SDS is present in the aqueous phase, the hydrophobic tails of the surfactant molecules associate with toluene while the negatively charged polar ends are retained within the water droplets. This creates the situation in which surfactant molecules self-align with all the negatively charged ends pointing toward the water droplets. As a means to minimize electrostatic repulsion between the confronting negative charges, the zeolite crystals within the water droplets consequently pack as closely as possible and self-align into a highly ordered form to minimize the surface area. At higher concentrations of SDS, the water droplets dispersed in toluene undergo deformation into anisotropic 3D structures as a result of the decrease of the surface energy. Therefore, in accordance with the irregular shapes of water droplets (templates), the zeolite nanocrystals assemble into highly anisotropic spherulites as depicted in Figure 2C. In strong support to the above Scheme, neutral surfactants, such as Triton X100, do not induce surface alignment within the resulting spherulites, regardless of the concentration. Cationic surfactants, such as dodecylpyridinium iodide and dodecyltrimethylammonium bromide, produce highly irregular interlinked aggregates (with no surface alignment) rather than producing discrete spherulites at concentrations higher than 1 mM.

The octahedral zeolite-X nanocrystals also readily yield microspherulites with random orientation of the crystals at the surface when surfactant-free water was employed as the aqueous phase dispersed in toluene (Fig. 1D). A 20 mM SDS solution employed instead of pure water again leads to production of microspherulites with highly ordered surfaces (Fig. 1E). At SDS < 20 mM, parts of the spherulites remain covered with randomly oriented outermost crystals. This result indicates that zeolite-X requires a higher concentration of negative charge.
on the surrounding toluene than zeolite-A for effective surface alignment and close packing. This may be attributed to the fact that the Si/Al ratio is higher for zeolite-X than zeolite-A (X: 1.48, A: 1.38), since zeolites with higher Si/Al ratios have lower negative charge densities on their surfaces. That an octahedron has higher number of facets (8) than a cube (6) may also affect the critical density of negative charges on each crystal needed for surface alignment. Production of anisotropic zeolite-X spherulites (Fig. 1F) also requires a higher concentration (50 mM) of SDS than that of zeolite-A.

Silica beads can also be assembled into anisotropic spherulites by use of SDS solution (4 mM) instead of pure water (Fig. 3B). For these neutral nanoparticles, even the cationic surfactants readily yield anisotropic 3D structures. The methodology was also tested for assembly of cylindrical zeolite-L into spherulites by use of pure water or SDS solutions at moderate concentrations (< 20 mM) (Fig. 3C). However, the cylindrical zeolite crystals do not align at the surfaces of spherulites even with the use of very high concentrations of SDS solutions (50 mM). This indicates that long cylindrical nanorods are not suitable for surface alignment.

For intermediate sonication periods (< 20 min), perforated spherulites are produced, as shown for the case of zeolite-A (Fig. 4). Perforation is more effective in the presence of SDS (4 mM). The degree of perforation generally decreases as the sonication time increases (compare Figs. 4A–D). For a given period of sonication (such as 5 min) however, the shapes and sizes of holes and the degrees of perforation are usually different from one spherulite to another in the same batch. The distribution of holes is also very random even within a spherulite, as shown in Figure 4A. The shaded spots on spherulites represent the internal voids covered with thin layers (usually monolayers) of zeolite (Figs. 4C,D). The 3D networks of the perforated spherulites can be seen from Figure 4E. Even the spherulites that appear to be void-free usually have internal voids within the spherulites, as shown in Figure 4H. Further study is necessary to gain control over the degree of perforation.

Overall, this work reports a novel strategy to align negatively charged nonspherical nanoparticles at the water–oil interface to a high degree of ordering. The concept presented here will be useful to prepare highly aligned mono- or bilayers of charged nonspherical nanoparticles along the 2D-phase inter-

Fig. 3. SEM images of spherulites that consist of either microscale silica beads or zeolite-L. A) A typical spherulite of silica bead showing the high surface ordering even at SDS = 0 mM. B) An anisotropic 3D assembly of silica beads with highly ordered outermost particles. SDS = 4 mM. C) A typical zeolite-L spherulite. SDS = 0 mM.

Fig. 4. A–D) SEM images of zeolite-A spherulites with different degrees of perforation, after A) 1, B) 3, C) 5, and D) 10 min sonication. E) An image of the 3D network of voids. F–H) Cross sections of spherulites with different degrees of perforation showing different shapes and networks.
faces between a very thin layer of water placed on an inert higher density oil phase. These highly perforated mesostructures of zeolite nanocrystals can be utilized as more effective catalysts and adsorbents than the conventional clay-bound aggregates, since the perforated microspheres allow easier molecular diffusion into their interiors (more data available from the authors).

**Experimental**

The procedures to prepare the zeolite microspheres [20–26] and silica beads [29] can be found elsewhere. For preparation of microspheres, cubic zeolite-A crystals (10 mg) were suspended in dry toluene (100 mL) contained in a tightly capped plastic bottle (200 mL). The lower half of the bottle was immersed in an ultrasonic bath (95 W, 28 kHz), and cooled to 4°C by use of an immersion cooler. The bottle containing the toluene suspension was first sonicated in the bath for 10 min to equilibrate the temperature and to evenly disperse the zeolite crystals in toluene. The plastic bottle was briefly removed from the bath and 40 μL of distilled deionized water was introduced into the toluene suspension. After recapping, the bottle was immersed again in the sonic bath and sonicated for additional 20 min or as desired. The bottle was removed from the bath and allowed to warm to room temperature (30 min on a bench). After equilibration to room temperature, the solution was poured onto a polycarbonate filter (1 μm pores) and the filtered zeolite aggregates were analyzed by scanning electron microscopy.

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**Self-Assembled Highly Ordered Spherical Mesoporous Silica/Gold Nanocomposites**

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There is a great deal of interest in the utilization of nanoscale particles of mesoporous silica in chromatography, drug delivery, photographic imaging, and pigmentation. [1–3] On the other hand microscale particles of mesoporous silica have been used as supports for nanoparticles of titanium dioxide, [4] cadmium(II) selenide, [5] rhodium oxide, [6] and silver, [7] with applications in areas such as catalysis, chemical sensing, nanoscale capacitors, and semiconductor devices. In one example, gold nanoparticles encapsulated in the aluminosilicate MCM-41 were found to show excellent catalytic activity in hydrogenation reactions. [8] In all the above examples, the nanoparticles were either encapsulated or grown within mesopore channels. Since the particle sizes are limited by channel geometry, which may be only a few nanometers in diameter, quantum confinement effects that perturb the nanoparticle properties are observed. In this work, we have pre-prepared a colloidal suspension of gold nanoparticles and use these as seeds for the propagation of a mesoporous shell. Therefore, size effects of the nanoparticles can be defined independently of the mesopore geometry. We show how to prepare monodisperse spherical mesoporous silica/gold nanocomposites smaller than 500 nm in diameter consisting of mesoporous silica and a single gold particle approximately 60 nm in diameter using a liquid-phase self-assembly process. Gold was chosen as the seed because there is a great deal of information on the preparation, stability and characterization of gold colloidal suspensions. [9]

There are a variety of self-assembly methods published on the synthesis of pure silica mesoporous spherical nanoparticles. [10–12] The procedures follow the Stöber method, [13] in which a silicate source, organic template and a morphological catalyst, for example ammonia, are mixed in stoichiometric amounts. These silica nanoparticles have properties analogous to MCM-41 powder [14] including highly-ordered mesopores, controlled pore size, and specific surface areas up to 1000 m²/g. The first nanoscale particles of mesoporous silica to contain gold nanoparticles were pre-

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