

Self-assembled mono- and multilayers of TMA-A zeolite nanocrystals on glass with triethoxysilane as covalent linkers

Young Mi Kim^a, Jeong Ho Chang^b and Ik Jin Kim^{a,*}

^a Institute for Processing and Application of Inorganic Materials, Department of Materials Science and Engineering, Hanseo University, Haemi- Myun, Seosan City, Chungnam 356-820, Korea

^b Korea Institute of Ceramic Engineering and Technology(KICET), 233-5, Gasan-Dong, Guencheon-Gu, Seoul 153-801, Korea

Well-organization of nano-sized zeolite crystals into uniformly oriented monolayers or multilayers on various substrates can be used as host materials for semiconductor clusters from 1 to 10 nm in diameter to generate specific electronic and optical properties. High-quality nano TMA-A zeolite crystals were synthesized using a hydrothermal method with a $\text{Al(i-pro)}_3 : 2.2 \text{ TEOS} : 2.4 \text{ TMAOH} : 0.3 \text{ NaOH} : 200\text{H}_2\text{O}$ composition. The average size of the zeolite crystal used was 130-150 nm with a lattice constant of 2.461 nm. The self-assembly mono- and multilayers of zeolite oriented with faces parallel to the glass substrates showed only the planes in the forms $\{h\ 0\ 0\}$ with triethoxysilane as covalent linkages. Environmental scanning electron microscopy (ESEM), high resolution transmission electron microscopy (HRTEM), and X-ray powder diffraction (XRD) were used to characterize the initial materials and the products obtained.

Key words: Zeolite, monolayer, surface treatment, nanocrystal, (3-Chloropropyl) Trimethoxysilane.

Introduction

Self-assembly of zeolite crystals in the form of highly oriented mono- and multilayers on various substrates is an effective way to organize building blocks into versatile functional entities. Well-oriented zeolite crystals have great potential as host materials for various semiconductor quantum dots(QDs), nonlinear optical molecules and as well-defined nanoreactors for the exploration of novel chemistries in highly ordered and oriented arrangements [1, 2]. At sizes of zeolite-encapsulated semiconductor QDs from 1 to 10 nm in diameter, they can in particular create electronic and optical properties specific to the form of a high flexible band gap energy [3, 4]. Therefore, the synthesis of perfect crystalline zeolite nanocrystals and the organization of these crystals into uniformly oriented monolayers on glass or ceramic substrates by covalent linkage is of great interest. Furthermore, stimulated by the great potential of zeolite monolayers, recently several novel covalent linkers have been devised with which they may be assembled on glass and ceramic substrates [5, 6]. While efforts to explore other novel covalent linkers should continue, simultaneous by efforts should also be made to achieve spatial organizations of zeolite monolayers on various substrates. This has the potential to provide attractive monolayers of microporous crystals with more useful

and versatile functional architectural types. For this propose, we first synthesized a single phase of TMA-A zeolite nano crystals using a hydrothermal method and a self-assembly monolayer coated onto glass substrates with triethoxysilane as covalent linkers.

Experimental Procedure

TMA-A zeolite nanocrystals of uniform particle sizes between 60-100 nm were synthesized using a hydrothermal method in a mother solution with a composition of $\text{Al(i-pro)}_3 : 2.2 \text{ TEOS} : 2.4 \text{ TMAOH} : 0.3 \text{ NaOH} : 200\text{H}_2\text{O}$ composition at 100 for three days. The reactant materials used were aluminum isopropoxide Al(i-pro)_3 (Aldrich, 98 wt%), tetraethylorthosilicate (TEOS, Aldrich, 98 wt%), tetramethylammonium hydroxide (TMAOH, Aldrich, 25 wt% in water), and sodium hydroxide (NaOH, Aldrich, 99.99 wt%). The autoclave was removed at predetermined times from the oven to arrest the reactions. The crystallized samples were collected and separated by centrifugation. The products were repeatedly dispersed in distilled water using ultra sonication and centrifugation as outlined above to remove the remaining mother solution until the pH of the dispersion was close to 7-8. (3-chloropropyl) triethoxysilane (CPS, 97%, Aldrich) was used as covalent linkages for the self assembly monolayer between zeolite and glass substrates. This organics was distilled and kept in a Schlenk storage flask under argon. The samples were obtained by drying at 80 °C for 4 h. The synthesized crystals and monolayer coated samples were characterized by XRD (Model RAD-2B, Rigaku Co.) with $\text{CuK}\alpha$ radiation, environmental scanning electron microscopy

*Corresponding author:
Tel :+82-41-660-1441
Fax:+82-41-688-4143
E-mail: ijkim@hanseo.ac.kr

(ESEM, XL-30, FEG), and high-resolution transmission electron microscopy (HRTEM, Tecnai G2, STEM).

Surface treatment of cover glass

Cover glasses ($18 \times 18 \text{ mm}^2$) were purchased from Marienfeld and treated in a piranha solution ($\text{H}_2\text{SO}_4 : 30\% \text{ H}_2\text{O}_2 = 3 : 1$) at $95\text{--}100^\circ\text{C}$ for 1 h to remove organic residues on the surface. The acid-treated glasses were washed with distilled water and dried at 120°C for 30 minutes before undergoing tethering steps with (3-chloropropyl) triethoxysilane, CPS. For tethering the CPS groups to the glass surface, CPS (0.5 ml) was injected into the toluene slurry using a hypodermic syringe with acid under a counter flow of N_2 gas and the mixture was refluxed for 1 h under N_2 gas at $110^\circ\text{C}/3 \text{ h}$. For this purpose, we prepared a glass incubation chamber consisting of a flat-bottomed cylinder (diameter = 20 cm, height = 20 cm) and a top lid (height = 3 cm) attached with a greaseless stopcock. The chamber was evacuated to $133.3 \mu\text{Pa}$ for 30 minutes at room temperature. The chamber was subsequently transferred into an oven whose temperature was maintained at 100°C and kept there for 15 minutes. After being cooled to room temperature, the glass plates with tethering CPS groups were removed from the chamber and washed with copious amounts of ethanol and finally with distilled water. The water-washed glass plates were dried by blowing them using a soft stream of N_2 gas. The dried glass plates were kept for 30 minutes in an oven at 110°C .

Assembly of TMA-A zeolite monolayer and multilayer

The zeolites were washed with copious amount of water until the wash solution was neutral. Centrifugation was necessary to separate the fine powders of zeolite from the aqueous slurry. The collected powders were successively washed with fresh toluene (100 ml) and ethanol (100 ml), and dried for 30 minutes in an oven at 120°C before assembly on the glass. To prepare the glass plates assembled with zeolite monolayers with CPS as the linkers, firstly dry toluene (50 ml) was introduced into a Schlenk flask containing TMA-A zeolite crystals under N_2 gas and the heterogeneous mixture was sonicated for 10 minutes in an ultrasonic cleaner to well disperse the zeolite particles evenly in the toluene. Secondly, the CPS tethered glass plates were introduced into a Schlenk flask containing the well-dispersed the zeolite powders in the toluene solution and then sonicated for 10 minutes in an ultrasonic cleaner to assemble the monolayer coatings. CPS groups bound to the glass surface readily react with surface hydroxyl groups of zeolite crystals according to Fig. 1. For multilayer coatings, the zeolite monolayer coated glasses were introduced into a CPS (0.5 ml) dispersed toluene solution and refluxed for 1 h under N_2 gas at 110°C for 3h, repeatedly. Subsequent tethered CPS groups on the zeolite-coated glass with dispersed zeolite crystals in the toluene solution led to easily assembly layer-by layer of zeolite crystals. The assembled zeolite powders

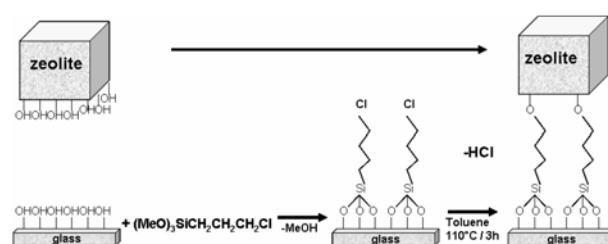


Fig. 1. (3-Chloropropyl) trimethoxysilane (CPS) group mounted on the top of the glass substrates via silane linkages.

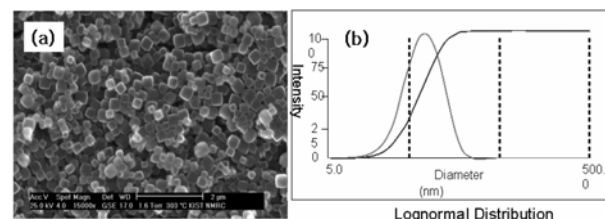


Fig. 2. SEM image of TMA-A zeolite nanocrystals (a) and particle size distribution for nano-TMA-A zeolite.

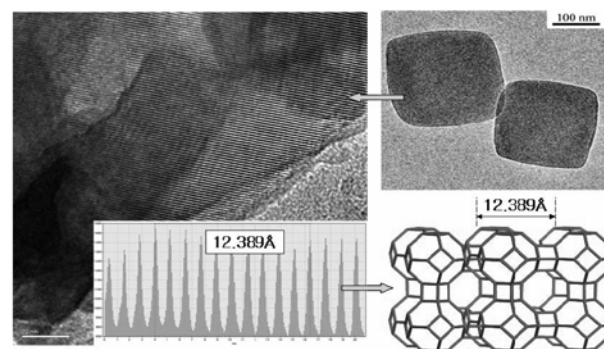


Fig. 3. HRTEM image and unit cell structure of TMA-A zeolite nanocrystals.

on the glass were successively washed with fresh toluene (100 ml) and ethanol (100 ml) and dried for 30 minutes in an oven at 120°C .

Results and Discussion

The morphology of the TMA-A zeolite crystals seen in a SEM image shows them to have cubic form comprised of well-controlled crystals of about 130 nm in size in a configuration having six planes, as shown in Fig. 2(a). Such images show both high crystallinity and perfect crystal morphology. The cube $\{001\}$ is composed of six perfect square faces that make angles of 90° . The particle size distribution can be estimated from low-magnification images and is further characterized by DLS (dynamic light scattering), as shown in Fig. 2(b). The DLS measurement of zeolite particle shows an average 130 nm in the size distribution, which is in agreement with the TEM observation as shown in Fig. 3. The resulting crystals of (a) were collected and separated by centrifugation with a relative centrifugal speed (rpm) of above 3,000.

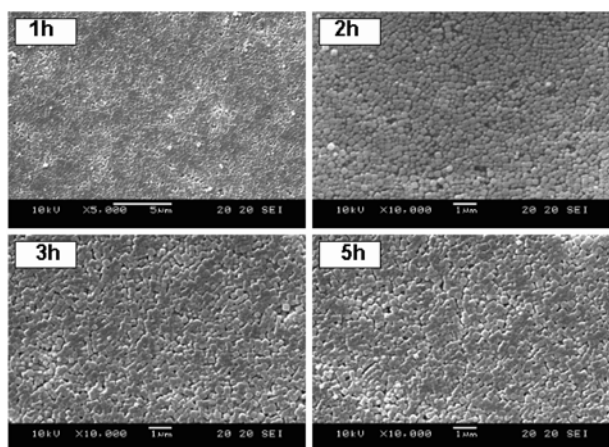


Fig. 4. Assembly of a monolayer of TMA-A zeolite by CPS as a function of reaction time.

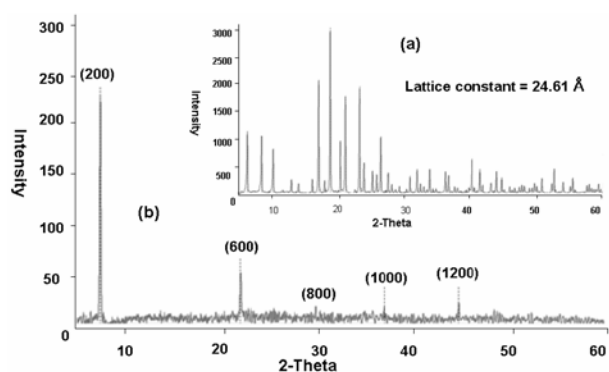


Fig. 5. X-ray powder diffraction patterns of TMA-A zeolite synthesized by a hydrothermal method (a) and a well-oriented self assembly monolayer zeolite using CPS as covalent linkages (b).

Fig. 3 shows an HRTEM image of a nanocrystal of the TMA-A zeolite. Such images show high degree of structural order and a perfect crystal morphology. It is clear from low-magnification images that the crystals have a typical cubic form with a range in edge size of approximately of 130 to 150 nm. In general, the framework of TMA-A zeolite crystals can be described in terms of two types of polyhedra; one has a simple cubic arrangement of eight tetrahedra and is termed D4R, and the other is a truncated octahedron of 24 tetrahedra or cages as previously described for the sodalite-type minerals [11]. The TMA-A zeolite is generated by placing the cubic D4R units in the center of the edges of a cube with an experimental lattice constant of 12.389 Å as shown in Fig. 3 [7]. These well-shaped zeolite crystals are excellent host materials having an ordered framework structure with regular cages and channels of sub-nano size (4Å) for semiconductor quantum dots (1-10 nm) [5].

Typical scanning electron microscope (SEM) images of the TMA-A zeolite monolayer assembled on a glass plate with CPS as the linker are shown in Fig. 4. All of the TMA-A zeolite crystals are oriented with a face parallel to the glass surface. Accordingly, the XRD patterns

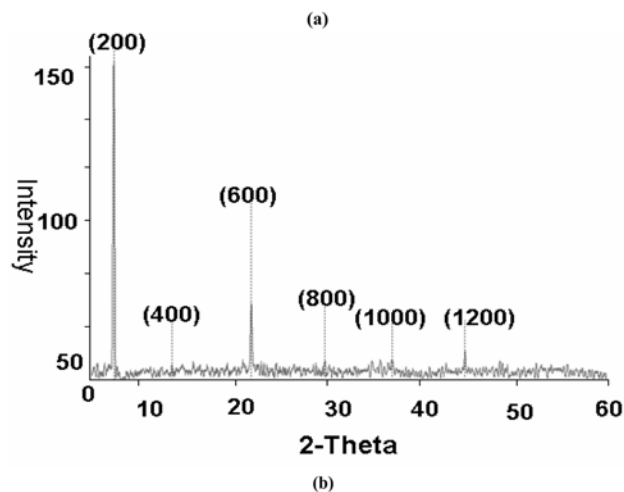
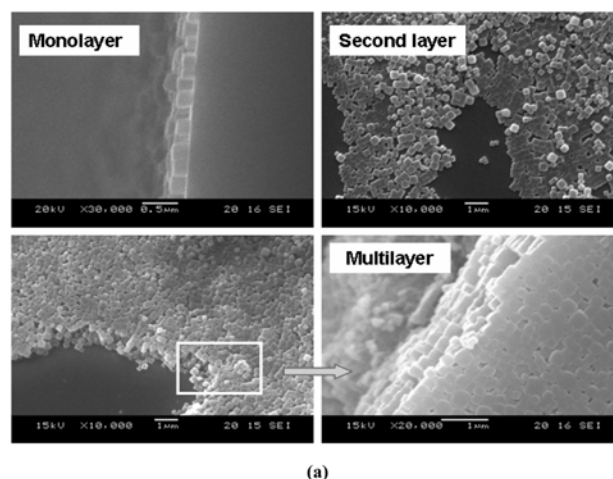


Fig. 6. Typical SEM images of monolayer, second layer, multilayers (a) and X-ray diffraction pattern of glass plates assembled with multilayers (b).

of the TMA-A zeolite-bound glass plates showed only five ($h\ 0\ 0$) lines at (200), (600), (800), (1000) and (1200) as shown in Fig. 5. Interestingly, the CPS-tethering zeolite crystals showed a tendency to pack closely despite the fact that the surface-lining groups are incapable of hydrogen bonding.

Fig. 6(a) shows typical SEM images of a monolayer, second layer, multilayers and a typical X-ray diffraction pattern of glass plates assembled with multilayers which revealed only (200) reflections regardless of the number of layers as shown in Fig. 6(b). However, the diffraction intensity increased with the number of layers in the multilayers.

Consistent with the SEM images, the measured X-ray diffraction patterns of the multilayer revealed the presence of diffraction lines that correspond to (200), (400), (600), (800), (1000), and (1200), due to the presence of well-oriented crystals, together with the ($h\ 0\ 0$) planes as shown in Fig. 6 (b). The diffraction lines from the ($h\ 0\ 0$) planes with $h = 2, 4, 6, 8, 10$, and 12 are likely to arise from the twinned crystals protruding from the parent TMA-A zeolite crystals with their a -axis perpendicular to a - c plane of the parent crystals. The appearance of

these ($h\ 0\ 0$) diffraction lines from the mono- and multilayers was not apparent from the synthesized zeolite powders as shown in Fig. 5(a).

Interestingly, the glass substrates modified with triethoxysilane(CPS) monolayers have been shown to give rise to highly oriented crystals of TMA-A zeolite with a family of $\{200\}$ planes. This phenomenon of close packing between the assembled TMA-A zeolite crystals is attributed to the surface migration of the weakly bound crystals [4]. These well-oriented porous films will be useful for the display devices industry for the next generation to provide an ideal media for the organization of semiconductor quantum dots necessary to develop novel optoelectronic and magnetic materials.

Conclusions

The crystal morphology of TMA-A zeolite is cubic and comprised of well-controlled crystals between 130 and 150 nm in size in a configuration having six perfect square planes and an average lattice constant of 24.61 Å. All of the TMA-A zeolite crystals are well oriented with a face parallel to the glass surface. Accordingly, the XRD patterns of the mono- and multilayer of TMA-A zeolite bound glass plates showed only five ($h\ 0\ 0$) lines with (200), (600), (800), (1000) and (1200). Interestingly, the CPS-tethered zeolite crystals showed a tendency to close pack despite the fact that the surface-lining groups are incapable of hydrogen bonding.

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