

# Ultrafast and Continuous Synthesis of Unaccommodating Inorganic Nanomaterials in Droplet- and Ionic Liquid-Assisted Microfluidic System

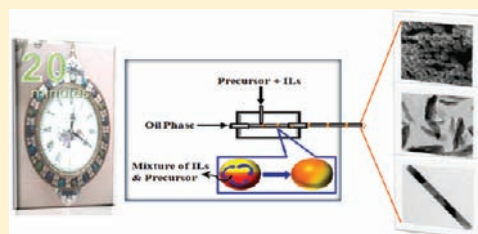
Phan Huy Hoang,<sup>†</sup> HoSeok Park,<sup>\*,§</sup> and Dong-Pyo Kim<sup>\*,†,‡</sup>

<sup>†</sup>National Creative Research Center of Applied Microfluidic Chemistry and <sup>‡</sup>Graduate School of Analytical Science and Technology, Chungnam National University, Daejeon 305-764, South Korea

<sup>§</sup>Department of Chemical Engineering, College of Engineering, KyungHee University, 1 Seochon-dong, Giheung-gu, Youngin-si, Gyeonggi-do 446-701, Korea

**S** Supporting Information

**ABSTRACT:** Despite many efforts on the synthesis of inorganic nanomaterials with uniform structure and narrow size distribution in a fast and continuous way, it is still a critical challenge in the chemistry research community due to the uncontrollable mass and heat transfer and the harsh experimental conditions of high temperature and pressure. Here we report a droplet- and ionic liquid-assisted microfluidic (DIM) synthesis method, which takes full advantage of both ionic liquids and droplet-assisted microreaction systems, for an ultrafast, mild, and continuous synthesis of various inorganic nanomaterials that takes only tens of minutes rather than days that are usually needed to synthesize. In particular, unaccommodating inorganic nanomaterials that are difficult to produce, such as nanoporous ZSM-5,  $\gamma$ -AlOOH, and  $\beta$ -FeOOH nanorods, were synthesized in only “20 minutes” of reaction time even with simple instrument. The DIM method delineated herein would offer a breakthrough synthetic approach for functional but unaccommodating inorganic nanomaterials in a continuous and mild manner.



## INTRODUCTION

At the heart of nanoscience and nanotechnology are nanostructured inorganic materials with unique properties and functions that can be used for a variety of applications.<sup>1</sup> Many efforts have been directed toward synthesizing nanostructured inorganic materials efficiently and obtaining their uniformity in bulk solution phase for wide applications.<sup>1</sup> Despite these intensive efforts, effective means for mass and heat transfer that are necessary to facilitate synthesis of inorganic nanomaterials with uniform shape and narrow size distribution<sup>2</sup> are yet to arrive. More problematic with crystalline inorganic nanoproducs, such as zeolite, is a long reaction time that typically lasts up to 1–2 days, even under hydrothermal conditions of high autogenous pressures up to 15 bar and high temperature in discontinuous batch processes.<sup>3,4</sup> Therefore, a breakthrough is needed for the synthesis of inorganic nanomaterials that allows fast process in a continuous manner under mild reaction conditions and yet results in uniform shape and narrow size distribution. The breakthrough would lead to wide applications in various fields by both academia and industry.

Recently, microfluidic synthesis has received much attention because of the advantages it offers, such as high surface area to volume ratio at the microscale, fast mass and heat transfer, and short diffusion distance.<sup>5</sup> Microreactors with continuous or discontinuous flow have been shown to efficiently produce mono-dispersed core–shell oxide, Au, or quantum dot nanoparticles,<sup>2,5–9</sup>

although there were problems associated with outgassing and clogging phenomena.<sup>2a,8b</sup> In particular, droplet-assisted microreactors offered rapid mixing of reactants and easy handling of solid reagents resulting in high-quality inorganic and hybrid nanoproducs.<sup>2,5–7,8a</sup>

Ionic liquids (ILs) have been shown to be very useful for applications involving solvents, catalysis, electrochemistry, separation, etc.<sup>10</sup> In particular, use of ILs as thermally stable, nonvolatile solvents, and/or templates was essential in preparing nanomaterials with simple reaction apparatus under mild conditions. For instance, nanoporous zeolite analogues and inorganic oxide nanoparticles were synthesized by bulk process in the presence of ILs under ambient pressure,<sup>4,11–15</sup> without the complications associated with high hydrothermal pressure in autoclave and postaddition of molecular or organic solvents. Although microwave synthesis in ILs is an efficient method to rapidly synthesize inorganic materials,<sup>14e,f</sup> delicate control in the burst heating and degradation of reactants is required.

We were, therefore, motivated that the breakthrough could be made by taking fully the advantages that are offered by both ILs and microfluidic droplet synthesis. Such a synthesis could open a new route for ultrafast and versatile synthesis of functional but unaccommodating inorganic nanomaterials that are difficult to

Received: June 16, 2011

Published: August 10, 2011

synthesize, such as silicate-based zeolites that have not yet been attempted by either ILs or microfluidic process.

Herein, we report an ultrafast, mild, and continuous synthesis of unaccommodating inorganic nanomaterials that takes only tens of minutes rather than days that are usually needed to synthesize. For the purpose, we devised and fabricated a droplet and IL-assisted microfluidic (DIM) system that does not require any sophisticated instruments and equipment. The basic strategy delineated in this work is to integrate ILs into droplet-based microreactors: the ILs as templates for the construction of nanostructures and also as thermally stable, nonvolatile solvents to resolve problems of microfluidic synthesis, and the droplet-based microreactors for rapid synthesis of uniform inorganic nanomaterials. Nanoporous zeolite and aluminum and iron hydroxide nanoparticles are chosen as target inorganic materials because of inability of the conventional technologies to construct the nanostructures in a short reaction time with uniform morphology and narrow size distribution, which would be a delightful innovation to the inorganic materials chemistry. The excellent quality of the materials thus synthesized is illustrated with ZSM-5 zeolite by testing the catalytic activity of the as-obtained zeolite for acetal formation reaction.

## ■ EXPERIMENTAL DETAILS

**DIM Synthesis of Silicate-Based ZSM-5 Zeolite.** The ZSM-5 zeolite particles were synthesized by the DIM method. The zeolite precursor solution was prepared by adding sodium aluminate ( $\text{NaAlO}_2$ ) to a homogeneous solution of mixture of 1-butyl-3-methylimidazolium chloride ( $\text{C}_4\text{MimCl}$ ) and deionized water. The solution of tetrapropylammonium hydroxide (TPAOH, 25% aqueous solution) and potassium hydroxide was added to the precursor solution. This solution was stirred for 1 h until completely dissolved. Then, tetraethyl orthosilicate (TEOS) as a silica source was added to the aforementioned aluminum precursor solution to prepare a solution with a mole ratio of the composition  $\text{TEOS}/\text{TPAOH}/\text{NaAlO}_2/\text{KOH}/\text{H}_2\text{O}/\text{C}_4\text{MimCl} = 8:1.05:0.1:0.85:64:20$ . The synthetic solution was obtained after aging for several hours (0–15 h) by stirring at room temperature, and used as a precursor solution of zeolite synthesis.

The zeolite precursor solution was forced into the continuous phase at the T-junction of the channel at flow rate of  $Q_d \mu\text{L min}^{-1}$  (flow rate 2–8  $\mu\text{L min}^{-1}$ ) to form the disperse phase. For the continuous phase, fluorocarbon oil (FC oil, 3M, St. Paul, MN) was introduced from the horizontal inlet at a flow rate of  $Q_c \mu\text{L min}^{-1}$  (flow rate 12–48  $\mu\text{L min}^{-1}$ ). Both the dispersed and continuous phases were injected into the microfluidic device using a syringe pump (PHD 2000, Harvard Instruments, Holliston, MA). Each droplet reactor was then flowed in the perfluoroalkoxyalkane (PFA) tube (i.d. 508  $\mu\text{m}$ ), which was immersed in a silicon oil bath at 150 °C, with different delay loop lengths of the PFA tube. The experiments were carried out at various flow rates of dispersed phase ( $Q_d$ ) and continuous phases ( $Q_c$ ) with constant ratio  $Q_d:Q_c = 1:6$ . After 5–20 min of reaction, the synthesized products were collected at the outlet of the PFA tube by a cooled vial at low temperature to avoid further crystallization. Then, the lower FC oil phase (continuous phase) was separated, and the synthesized products were collected by centrifuging (11 000 rpm, 15 min). After washing the as-obtained samples with acetonitrile and deionized water by three repetitions to remove the excess ionic liquids, the resultant products were dried at 100 °C for several hours for analysis of samples by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and dynamic light scattering (DLS). Owing to the fast heat release of microfluidic system for quenching of reaction, the as-collected samples were not gel-like but in a colloidal state with respect to the chemical

compositions. Finally, the resultant products was converted into the H-form by ion exchanges by treating three times with a solution of  $\text{NH}_4\text{NO}_3$  1 M at 60 °C and followed by washing with DI water, drying at 100 °C, and calcination in air at 550 °C for 6 h.

In order to examine effectiveness of DIM process on aging step, the DIM system for continuous aging and reaction step in PFA capillary tube were fabricated by assembling a lab-on-a-chip part for droplet generation at T-junction and second part of PFA capillary tube for aging step at room temperature and reaction step at high temperature (see Figure S1, Supporting Information). The synthetic solution was prepared similarly to the above-mentioned procedure except without aging step.

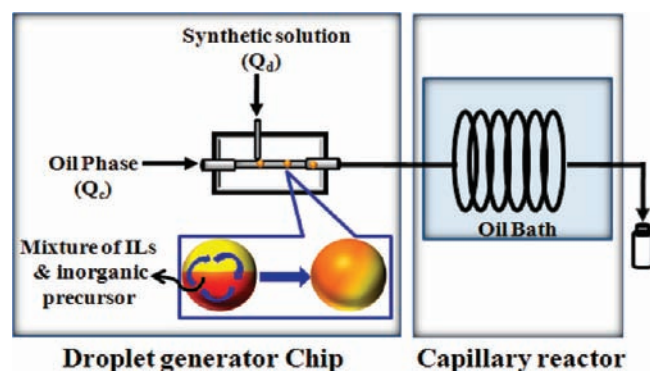
**DIM Synthesis of Aluminum Hydroxide ( $\gamma$ - $\text{AlOOH}$ ).**  $\text{C}_4\text{MimCl}$  (1.4 g) was mixed with 3 mL of an aqueous solution of 0.1 M HCl. After that 1.96 g of aluminum chloride hexahydrate was added to above solution. The resultant mixture was stirred at 60 °C for 2 h, followed by aging at 60 °C for several hours. To complete crystallization and induce the formation of boehmite structure, the mixture was synthesized at ambient pressure through a DIM process by following the same procedure as ZSM-5 except for the temperature set at 130 °C. The synthesized products were collected at the outlet of the PFA tube, purified by centrifuging, and washed with acetonitrile and deionized water. The obtained  $\gamma$ - $\text{AlOOH}$  product was transformed into  $\gamma$ - $\text{Al}_2\text{O}_3$  at 550 °C in air for 3 h.

**DIM Synthesis of Iron Hydroxide ( $\beta$ - $\text{FeOOH}$ ).** In 1 mL of deionized water, 1.222 g of  $\text{C}_4\text{MimCl}$  was mixed. After 1.89 g of ferric chloride hexahydrate was added to the mixture at the molar ratio of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  to  $\text{C}_4\text{MimCl}$  of 1:1, 3 mL of 0.1 M HCl was added to the resulting mixture dropwise to control to a pH of 3. The resultant mixture was stirred at room temperature for 2 h in order to obtain a homogeneous solution. To induce the formation of nanorod iron hydroxide via a green ionothermal process, the mixture was synthesized at ambient pressure through a DIM process by following the same procedure as the boehmite synthesis in droplet. The synthesized products were collected at the outlet of the PFA tube, purified by centrifuging, and washed with acetonitrile and deionized water.

**Catalytic Reaction.** The catalytic reactions were carried out in a three-necked flask equipped a reflux condenser under  $\text{N}_2$  atmosphere. The molar ratios of benzaldehyde with ethylene glycol and 1-butanol were 1:2 and 1:4, respectively. In particular, benzaldehyde (1.06 g, 0.05 mol), ethylene glycol (1.24 g, 0.1 mol), or *n*-butyl alcohol (2.96 g, 0.2 mol) and the calcined ZSM-5 catalyst (0.05 g) were mixed under continuous stirring. The mixture was kept stirring at reaction temperature of 80 °C for several hours. In the acetal formation reaction of benzaldehyde with glycol or *n*-butyl alcohol, reactions were continued until the equilibrium. The samples were analyzed by NMR to calculate the conversion of reactants.

## ■ RESULTS AND DISCUSSION

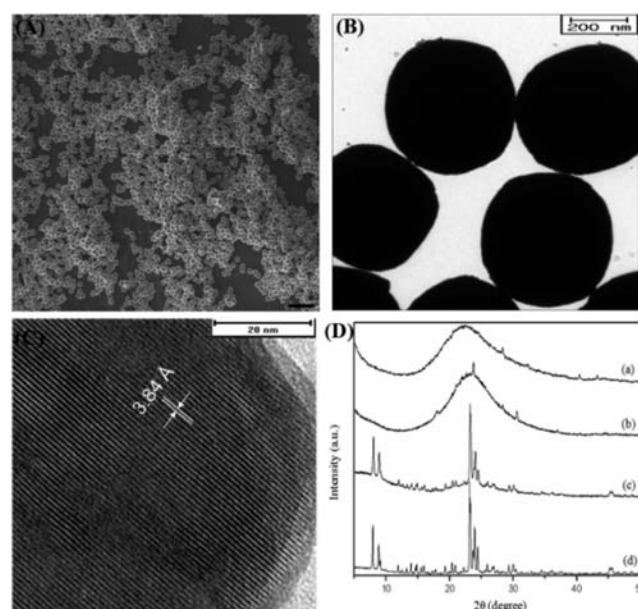
**Set up For a DIM System.** Figure 1 illustrates the synthetic procedure of inorganic nanomaterials using a DIM system. The fluoropolymer lab-on-a-chip with multisized channels was fabricated by a simple, cost-effective single-step method as previously reported by our group.<sup>16</sup> The DIM system was assembled with a solvent resistant and thermally stable fluoropolymer (FP) lab-on-a-chip part for droplet generation at T-junction and a capillary perfluoroalkoxyalkane tube (PFA, 60–180 cm, i.d. 508  $\mu\text{m}$ ) part for the extended reaction at high temperature. Inorganic precursors were dissolved in ILs and then were encapsulated in nanoliter droplets (see Figure S2, Supporting Information) at the T-junction. Droplets passed through the PFA tube (i.d. 508  $\mu\text{m}$ ) of a microreactor that is immersed in a silicon oil bath, which was heated up to the desired temperature (130–150 °C).



**Figure 1.** Illustration of the DIM system for synthesis of various inorganic nanomaterial.

The resident time of droplet was controlled by the loop length (60–180 cm) of the PFA tube. In particular, neither back pressure nor clogging in microfluidic system occurred even in the absence of any instrument, such as pressure regulator and high-pressure pump, because of the negligible vapor pressure and thermal stability of ILs. Moreover, the stable device operation was achieved even at high temperature ( $\approx 150\text{ }^{\circ}\text{C}$ ). In this regard, the DIM synthesis method provides a convenient, safe, fast, and controllable approach for the preparation of inorganic nanomaterials.

**Ultrafast and Continuous Synthesis of ZSM-5 Zeolite in a DIM System.** The DIM method is first demonstrated here by applying it to the synthesis of silicate-based ZSM-5 zeolite. Although there were significant reports on successful bulk syntheses of aluminophosphate zeolite analogues using ILs in the form of powder and film,<sup>4,11,12</sup> there were very few examples for aluminosilicate- or silicate-based zeolite synthesis due to the limited solubility of silica precursors (TEOS) in the common ILs.<sup>4</sup> The enhanced solubility of TEOS, attributable to the use of water as cosolvent and the presence of ion hydroxide in reaction media,<sup>4a</sup> enabled to synthesize uniform ZSM-5 products via a solution crystallization in a DIM process.<sup>11</sup> Hydrophilic  $\text{C}_4\text{MimCl}$  IL was used as a cosolvent and a suppressor of vapor pressure of water. In addition, compartmentalization of synthetic solution in droplets assisted the prevention of water evaporation due to the confinement effect.<sup>7a</sup> The ZSM-5 was successfully synthesized with the DIM method only within 15 min of reaction time, much faster than several hours of bulk reaction as previously reported.<sup>17</sup> Along with the ultrafast synthesis, ZSM-5 revealed uniform morphology and narrow size distribution, with a diameter of  $380 \pm 20\text{ nm}$ , as shown in Figure 2. Furthermore, high crystallinity and purity of ZSM-5 was confirmed by XRD patterns, which were assigned to the orthorhombic structure (JCPDS 44–0002) (see Figure S3, Supporting Information). The crystalline structure of ZSM-5 was observed in an HR TEM image, showing interplanar spacings of  $3.838\text{ \AA}$  corresponding to the (501) plane. The crystalline size of  $386\text{ nm}$ , calculated by the Scherrer's equation, was reasonably consistent with the average particle size observed from SEM image. The crystalline size and crystallinity of ZSM-5 was controlled by manipulating the reaction time with loop length or flow rate. With respect to the textural properties, the ZSM-5, calcined at  $550\text{ }^{\circ}\text{C}$  in air, has a pore volume of  $0.46\text{ cm}^3\cdot\text{g}^{-1}$ , a surface area of  $408\text{ m}^2\cdot\text{g}^{-1}$ , and a pore size of  $\approx 3\text{ nm}$  as determined by Brunauer-Emmert-Teller (BET) analysis (see Figure S4, Supporting Information). It is postulated that the hydrophilic ILs interact with the primary

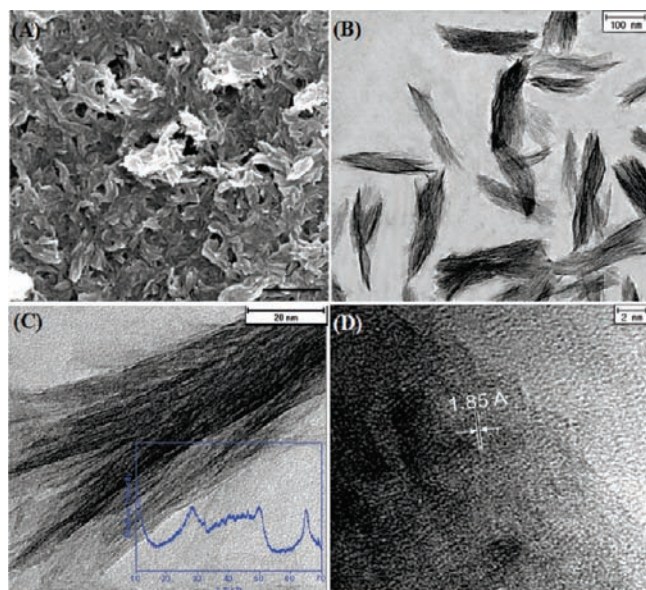


**Figure 2.** (A) SEM ( $2\text{ }\mu\text{m}$  bar) images of ZSM-5, (B) TEM ( $200\text{ nm}$  bar) and (C) HRTEM ( $20\text{ nm}$  bar) images of ZSM-5 obtained by DIM process in 20 min of residence time, (D) XRD patterns of ZSM-5 for four different residence times of (a) 5, (b) 10, (c) 15, and (d) 20 min.

aluminosilicate crystals through the hydrogen bonding-co- $\pi$ - $\pi$  stacking and as a result, the interactions lead to aggregation and organization into mesoporous zeolite crystals.<sup>15</sup> Consequently, ZSM-5 with uniform size, high crystallinity, and large surface area was very rapidly and readily synthesized through the DIM synthesis.

In order to assess the advantages offered by the DIM method, three control experiments were performed: experiment with the DIM system without IL, the same experiment only with capillary reactor, and that with flask or bulk phase synthesis. In addition to the role of cosolvent played by IL, it is also capable of retaining a sufficient amount of water at high temperature by suppressing the vapor pressure.<sup>4b</sup> In the absence of IL, the DIM device did not work due to the occurrence of high back pressure and clogging. These findings indicate that the use of IL is crucial for overcoming the operation problem of microfluidic system in synthesizing nanoporous ZSM-5. For comparison, ZSM-5 was also synthesized by capillary continuous microreactor and bulk phase reaction, under the same chemical composition and reaction temperature as in ZSM-5 prepared through the DIM method. In the case of continuous microreactor systems without droplet generators, ZSM-5 showed irregular shape, wider size distribution and lower crystallinity. Besides, the crystallinity of ZSM-5 was comparable to that of ZSM-5 prepared through bulk reaction that took 24 h but with much higher uniformity (see Figure S5–S7, Supporting Information). It is worth noting that a DIM process integrated by ILs and droplet microfluidics induces the uniform and high crystalline zeolite nanoparticles by effectively regulating their growth even with simple instrumentation.

It is reported that the aging step of the synthetic solution at room temperature is useful for reducing the crystallization time.<sup>18</sup> The bulk reaction for 24 h without aging step produced nearly amorphous ZSM-5 with a broad XRD peak (Figure S8a, Supporting Information). Then the effectiveness of DIM process on aging step was examined by performing continuous aging and

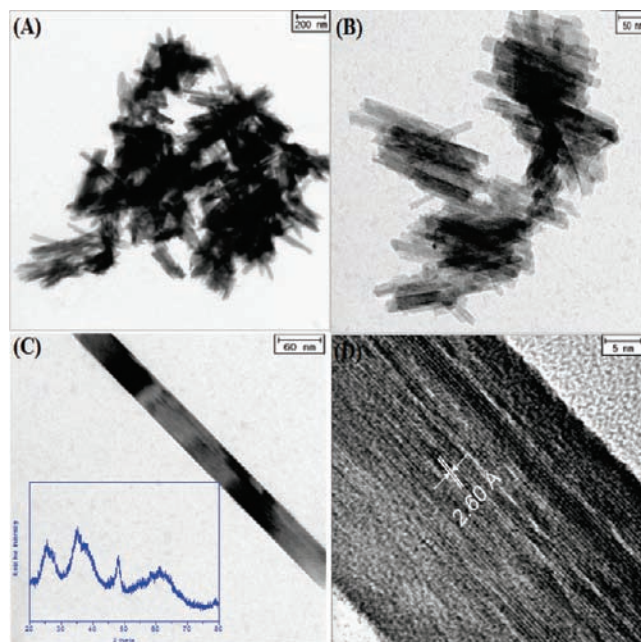


**Figure 3.** (A) SEM image (500 nm bars) of  $\gamma$ -AlOOH obtained by DIM process in 17 min of residence time, and TEM images of  $\gamma$ -AlOOH (B) scale bar of 100 nm, (C) scale bar of 20 nm (inset is the XRD pattern of  $\gamma$ -AlOOH), and (D) HR-TEM image with scale bar of 2 nm.

reaction step in PFA capillary tube (Figure S1, Supporting Information), in comparison to different aging times in bulk phase. The comparative X-ray diffraction (XRD) spectra of Figure S8b and c, Supporting Information reveal that 20 min aging in the droplet corresponds to 5 h aging in bulk phase. It indicates that droplet was also effective to promote the nucleation during the aging step as well as the growth of zeolite nanoparticle.

The reaction mixture confined in discrete droplets on a nanoliter scale that move along the channel gets homogenized quickly in chemical composition and temperature through efficient heat transfer and chaotic advection in the droplets that enhances greatly the degree of mixing. Moreover, high surface area to volume ratio of droplet would result in rapid heat and mass transfer in crystallization.<sup>7a,16</sup> It is apparent that the crystallization in droplets occurred very fast, within a short residence time of minutes, and this fast crystallization could lead to narrow particle-size distribution with high crystallinity. The synthesis of high-quality ZSM-5 is ultrafast in the sense that the synthesis by DIM takes 15 min, whereas it takes 1 day or 24 h with bulk phase reaction. And it is well-known that the crystallization process is strongly influenced by kinetics in nucleation and growth steps. Considering that the crystallization described herein is a diffusion controlled system rather than a reaction controlled system due to the fast reaction rates of precursors used in these syntheses of inorganic nanomaterials,<sup>19</sup> the crystallization in the nanoliter-scale droplet was facilitated by the enhanced mass transfer with a short diffusion distance. In other words, the chaotic advection in the droplet flow might promote efficiently the probability of a solute molecule to come into contact with an existing crystal. In addition, it is believed that the fast heat transfer in a DIM system enabled to supply rapidly thermal energy for the burst nucleation and the subsequent crystal growth with less lattice defects.

**Versatile Synthesis of Inorganic Nanomaterials in a DIM System.** In order to demonstrate the versatility of this approach for the synthesis of unaccommodating inorganic materials, boehmite



**Figure 4.** TEM image of  $\beta$ -FeOOH nanocrystals obtained by DIM process in 15 min of residence time: (A) scale bar of 200 nm, (B) scale bar of 50 nm, (C) scale bar of 60 nm (inset is XRD pattern of  $\beta$ -FeOOH nanocrystals), and (D) HRTEM image with scale bar of 5 nm.

( $\gamma$ -AlOOH) as a precursor of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and iron hydroxide ( $\beta$ -FeOOH) as a precursor of iron-based materials were synthesized by the DIM process. Although  $\gamma$ -AlOOH is regarded as an advanced material owing to its excellent catalytic and textural characteristics, it is very difficult to form the nanostructure due to fast reaction rates of precursors and harsh synthetic conditions.<sup>19</sup> As was the case with the synthesis of ZSM-5,  $\gamma$ -AlOOH with uniform nanostructures was rapidly synthesized only in 17 min, which is the fastest synthetic time ever reported. As shown in Figure 3,  $\gamma$ -AlOOH was assembled into well-aligned bundles consisting of nanofibers with diameters of 1–3 nm and lengths of 120–188 nm. The crystalline structures of  $\gamma$ -AlOOH were identified to be the typical orthorhombic boehmite phase (JCPDS 21-1307). The broad XRD patterns of  $\gamma$ -AlOOH are attributed to the small size of the nanocrystalline domains, as shown in the high-resolution transmission electron microscopy (HR-TEM) image (Figure 3D). The observation of the lattice resolved fringes of  $\gamma$ -AlOOH, which displayed a constant spacing of about 1.85 Å corresponding to that of the (200) planes, indicates the existence of a crystalline framework and the preferential orientation of specific crystalline planes. The orientation of the bunches of nanofibers was derived from the interactions in play on the surface of the individual nanofibers as previously reported.<sup>13d</sup> In a manner analogous to the IL-templated system in bulk phase, ILs played the role of cosolvent and templating agent during the thermal treatment in microreactors for the construction of  $\gamma$ -AlOOH nanostructures. Furthermore, it was confirmed that the topochemical transformation of  $\gamma$ -AlOOH into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> occurred during dehydration and deoxygenation at 550 °C.<sup>13c,d</sup>

Another unaccommodating nanomaterial of  $\beta$ -FeOOH nanocrystals was also synthesized by the DIM method using the identical C<sub>4</sub>MimCl IL. The structures and the crystalline phases of  $\beta$ -FeOOH are shown in the TEM images and XRD pattern given in Figure 4. Nanorods of  $\beta$ -FeOOH with a diameter of

40 ± 5 nm and a length of 400 ± 20 nm were constructed only in 15 min of reaction time. The XRD peaks of β-FeOOH nanorods were assigned to the tetragonal crystalline phase (JCPDS 34-1266). The lattice resolved fringes of β-FeOOH nanorods with a constant spacing of 2.60 Å correspond to the (400) planes, as confirmed by TEM and XRD results, which means that β-FeOOH nanorods were preferentially grown along a specific direction of the Z axis with the minimization of surface energy. The findings attest to the solvent and templating effects of ILs on the formation of nanostructures in droplet-based microreactors. These results confirm that the DIM method is an innovative synthetic route to nanostructured inorganic oxides, which is ultrafast and versatile without any rate-controlling agents.

**Catalytic Reaction.** ZSM-5 is one of the most important catalysts in organic synthesis and in oil refining process, owing to its high-surface area, shape selectivity, and strong acidity. Therefore, acetal formation reaction was chosen to test the quality of the ZSM-5 zeolite catalyst synthesized by DIM. As can be seen in Table S1, Supporting Information, the as-prepared ZSM-5 shows 53.6% and 71.8% conversion yields of benzaldehyde when reacted with 1-butanol and glycol, respectively, which are significantly higher than 30.4% and 52.9% yielded by the conventional ZSM-5. The highly improved catalytic performance of the zeolite obtained from DIM could be ascribed to the large number of active sites on the high surface area as well as the presence of mesopore that is an important factor in the acetal formation with large size reactant molecules, such as benzaldehyde.<sup>17b</sup>

## CONCLUSION

In summary, an ultrafast and continuous synthesis method has been presented for those unaccommodating nanomaterials that are difficult to synthesize because of a long reaction time that can last up to days even at high pressure and temperature. The droplet- and ionic liquid-assisted microfluidic (DIM) system devised and fabricated in this work enables a reduction of reaction time from days to tens of minutes, allows mild reaction conditions, and yet produces narrow size distribution and excellent crystalline qualities. Three unaccommodating nanomaterials have been synthesized with the DIM system to fully demonstrate the advantages offered by the synthesis method with excellent results. In particular, ZSM-5 zeolite nanomaterial, which is an important catalyst, was synthesized by the method and delivered a performance superior to the conventionally synthesized catalyst. The synergistic combination of ionic liquid and droplet microfluidic process allows for ultrafast and continuous synthesis of various inorganic nanomaterials, which greatly expands the utility and the versatility of this approach for the synthesis of alternative nanomaterials.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental details, Table S1, and Figure S1–S8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

[dpkim@cnu.ac.kr](mailto:dpkim@cnu.ac.kr); [phs0727@khu.ac.kr](mailto:phs0727@khu.ac.kr)

## ACKNOWLEDGMENT

This study was funded by the 2008 Creative Research Initiative Program [R16-2008-138-01000-0(2008)] administered by the Korean Ministry of Education, Science, and Technology.

## REFERENCES

- (1) (a) Van Bommel, K. J.; Friggeri, C. A.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 980. (b) Cushing, B. L.; Kolesnichenko, V. L.; O'Connor, C. J. *Chem. Rev.* **2004**, *104*, 3893. (c) Jun, Y.; Choi, J.; Cheon, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 3414.
- (2) (a) Abou-Hassan, A.; Sandre, O.; Cabuil, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 6268. (b) Duraiswamy, S.; Khan, S. A. *Small* **2009**, *5*, 2828.
- (3) (a) Cundy, C. S.; Cox, P. A. *Chem. Rev.* **2003**, *103*, 663. (b) Morris, R. E.; Weigel, S. J. *Chem. Soc. Rev.* **1997**, *26*, 309.
- (4) (a) Morris, R. E. *Chem. Commun.* **2009**, 2990. (b) Cai, R.; Liu, Y.; Gu, S.; Yan, Y. *J. Am. Chem. Soc.* **2010**, *132*, 12776.
- (5) (a) The, S. Y.; Lin, R.; Hung, L. H.; Lee, A. P. *Lab Chip* **2008**, *8*, 198. (b) Hung, L. H.; Choi, K. M.; Tseng, W.-Y.; Tan, Y.-C.; Shea, K. J.; Lee, A. P. *Lab Chip* **2006**, *6*, 174.
- (6) (a) Frenz, L.; El Harrak, A.; Pauly, M.; gin-Colin, S. B.; Griffiths, A. D.; Baret, J.-C. *Angew. Chem., Int. Ed.* **2008**, *47*, 6817. (b) Shum, H. C.; Abate, A. R.; Lee, D.; Studart, A. R.; Wang, B.; Chen, C. H.; Thiele, J.; Shah, R. K.; Krummel, A.; Weitz, D. A. *Macromol. Rapid Commun.* **2010**, *31*, 108. (c) Pan, Y. C.; Ju, M. H.; Yao, J. F.; Zhang, L. X.; Xu, N. P. *Chem. Commun.* **2009**, 7233. (d) Pan, Y. C.; Yao, J. F.; Zhang, L. X.; Xu, N. P. *Ind. Eng. Chem. Res.* **2009**, *48*, 8471.
- (7) (a) Song, H.; Chen, D. L.; Ismagilov, R. F. *Angew. Chem., Int. Ed.* **2006**, *45*, 7336. (b) Li, W.; Pham, H. H.; Nie, Z.; MacDonald, B.; Gunther, A.; Kumacheva, E. *J. Am. Chem. Soc.* **2008**, *130*, 9935. (c) Shestopalov, I.; Tice, J. D.; Ismagilov, R. F. *Lab Chip* **2004**, *4*, 316. (d) Chan, E. M.; Alivisatos, A. P.; Mathies, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 13854. (e) Song, Y.; Hormes, J.; Kumar, C. S. S. R. *Small* **2008**, *4*, 698. (f) Hassan, A. A.; Sandre, O.; Cabuil, V.; Tabeling, P. *Chem. Commun.* **2008**, 1783.
- (8) (a) Yen, B. K. H.; Gunther, A.; Schmidt, M. A.; Jensen, K. F.; Bawendi, M. G. *Angew. Chem., Int. Ed.* **2005**, *44*, S447. (b) Yen, B. K. H.; Stott, N. E.; Jensen, K. F.; Bawendi, M. G. *Adv. Mater.* **2003**, *15*, 1858.
- (9) (a) Marre, S.; Park, J.; Rempel, J.; Guan, J.; Bawendi, M. G.; Jensen, K. F. *Adv. Mater.* **2008**, *20*, 4830. (b) Marre, S.; Baek, J.; Park, J.; Bawendi, M. G.; Jensen, K. F. *J. Assoc. Lab. Auto.* **2009**, 367. (c) Kawanami, H.; Matsushima, K.; Sato, M.; Ikushima, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5129.
- (10) (a) Zhang, S. J.; Sun, N.; He, X. Z.; Lu, X. M.; Zhang, X. P. *J. Phys. Chem. Ref. Data* **2006**, *35*, 1475. (b) Andrade, C. K. Z. L.; Alves, M. *Curr. Org. Chem.* **2005**, *9*, 195. (c) Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459. (d) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773. (e) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
- (11) Cooper, E. R.; Andrews, C. D.; Wheatley, P. S.; Webb, P. B.; Wormald, P.; Morris, R. E. *Nature* **2004**, *430*, 1012.
- (12) (a) Morris, R. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 442. (b) Cai, R.; Sun, M. W.; Chen, Z. W.; Munoz, R.; O'Neill, C.; Beving, D. E.; Yan, Y. S. *Angew. Chem., Int. Ed.* **2008**, *47*, 525.
- (13) (a) Park, H. S.; Lee, Y. C.; Choi, B. G.; Cho, Y. S.; Yang, J. W.; Hong, W. H. *Chem. Commun.* **2009**, 4058. (b) Park, H. S.; Choi, Y. S.; Kim, Y. J.; Hong, W. H.; Song, H. J. *Adv. Funct. Mater.* **2007**, *17*, 2411. (c) Park, H. S.; Yang, S. H.; Jun, Y. S.; Hong, W. H.; Kang, J. K. *Chem. Mater.* **2007**, *19*, 535. (d) Park, H. S.; Lee, Y. C.; Choi, B. G.; Hong, W. H.; Yang, J. W. *ChemSusChem* **2008**, *1*, 356.
- (14) (a) Parnham, E. R.; Drylie, E. A.; Wheatley, P. S.; Slawin, A. M. Z.; Morris, R. E. *Angew. Chem., Int. Ed.* **2006**, *45*, 4962. (b) Parnham, E. R.; Morris, R. E. *J. Am. Chem. Soc.* **2006**, *128*, 2204. (c) Ma, H. J.; Tian, Z. J.; Xu, R. S.; Wang, B. C.; Wei, Y.; Wang, L.; Xu, Y. P.; Zhang, W. P.; Lin, L. W. *J. Am. Chem. Soc.* **2008**, *130*, 8120. (d) Wang, L.; Xu, Y. P.; Wei, Y.; Duan, J. C.; Chen, A. B.; Wang, B. C.; Ma, H. J.; Tian, Z. J.; Lin, L. W. *J. Am. Chem. Soc.* **2006**, *128*, 7432. (e) Xu, Y. P.; Tian, Z. J.; Wang, S. J.; Hu, Y.; Wang, L.; Wang, B. C.; Ma, Y. C.; Hou, L.; Yu,

J. Y.; Lin, L. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 3965. (f) Zhu, Y. J.; Wang, W. W.; Qi, R. J.; Hu, X. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1410.

(15) (a) Zhou, Y.; Schattka, J. H.; Antonietti, M. *Nano Lett.* **2004**, *4*, 477. (b) Ma, Z.; Yu, J.; Dai, S. *Adv. Mater.* **2010**, *22*, 261.

(16) Hoang, P. H.; Nguyen, C. T.; Perumal, J.; Kim, D. P. *Lab Chip.* **2011**, *11*, 329.

(17) (a) Argauer, R. J.; Landolt, G. R. US Patent 3702886, 1972. (b) Zhao, J.; Zhou, J.; Chen, Y.; He, Q.; Ruan, M.; Guo, L.; Shi, J.; Chen, H. *J. Mater. Chem.* **2009**, *19*, 7614.

(18) (a) Slangen, P. M.; Jansen, J. C.; van Bekkum, H. *Microporous Materials* **1997**, *9*, 259. (b) Thompson, R. W. Recent advance in the understanding of zeolite synthesis. In *Molecular Sieves: Science and Technology: Synthesis*; Karge, H.G., Weitkamp, J., Eds.; Springer: Berlin, Germany, 1998; pp 1–33.

(19) Cabrera, S.; Haskouri, J. E.; Alamo, J.; Beltrán, A.; Beltrán, D.; Mendioroz, S.; Marcos, M. D.; Amorós, P. *Adv. Mater.* **1999**, *11*, 379.