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Published on Web 02/16/2007

Biomimetic and Aggregation-Driven Crystallization Route for Room-Temperature Material Synthesis: Growth of β-Ga_2O_3 Nanoparticles on Peptide Assemblies as Nanoreactors

Sang-Yup Lee,† Xueyun Gao, and Hiroshi Matsui*

Contribution from the Department of Chemistry, Hunter College, and The Graduate Center, The City University of New York, 695 Park Avenue, New York, New York 10021

Received November 2, 2006; E-mail: hmatsui@hunter.cuny.edu

Abstract: The room-temperature synthesis of β-Ga_2O_3 nanocrystal was examined by coupling two biomimetic crystallization techniques, enzymatic peptide nanoassembly templating and aggregation-driven crystallization. The catalytic template of peptide assembly nucleated and mineralized primary β-Ga_2O_3 crystals and then fused them to grow single-crystalline and monodisperse nanoparticles in the cavity of the peptide assembly at room temperature. In this work, the peptide assembly was exploited as a nanoreactor with an enzymatic functionality catalyzing the hydrolysis of gallium precursors. In addition, the characteristic ring structure of peptide assembly is expected to provide an efficient dehydration pathway and crystallization control over the surface tension, which are advantageous for β-Ga_2O_3 crystal growth. This multifunctional peptide assembly could be applied for syntheses of a variety of nanomaterials that are kinetically difficult to grow at room temperature.

Recently, nanostructured semiconductor oxides have been attracting a great deal of attention for their potential uses in optoelectronic and sensor applications.[1−3] In particular, monoclinic gallium oxide, β-Ga_2O_3, has been studied extensively because of the wide band gap that provides light emission in a broad range. In general, oxide semiconductor materials are synthesized at high temperature.[4] However, if these syntheses can be conducted in milder conditions such as room temperature, it reduces the production cost, the facility size (such as cooling systems), and the manpower, which will have a significant impact on manufacturing gallium-based nanodevices. Low-temperature processing could also lead to reduced nanoparticle aggregations and defects induced from local thermal stresses. Here, the monodisperse gallium oxide semiconductor crystals, which are known to be kinetically unfavored to grow in ambient conditions, were synthesized at room temperature by coupling two biomimetic crystallization techniques, enzymatic peptide nanoassembly templating and aggregation-driven crystallization. The term aggregation-driven crystallization is defined as a process in which a single crystal is grown by aggregation in an aligned manner and the fusion of primary nanoparticles.[5] The peptide assembly used in this study captured the nucleated primary particles, mineralized them to β-Ga_2O_3 crystals by its catalytic functions, and then fused them to grow single-crystalline and monodisperse nanoparticles in the cavity of the peptide assembly at room temperature.

Biological systems possess the function to synthesize exotic materials at room temperature via their enzymatic activities. Recently various room-temperature material syntheses were examined by use of biomimicked systems engaging biomineralization.[6−14] Those biomolecular catalysts, dictated by the genetic code and protein assembly, can facilitate mineralizations via specific interactions between chemical moieties in unique conformations and solutes. This specific interaction that stabilizes and controls the kinetics of the intermediate phases during the synthesis leads to yield in unique crystal structures.[15] Although enzymes in nature can mineralize metals and semiconductors whose growths are hardly achieved at room temperature, those enzymes are not exactly designed to grow them in uniform size and shape. For example, silicatein moieties, the silica skeletal elements of a marine sponge, were applied to catalyze the hydrolysis and polycondensation of γ-Ga_2O_3.[15] In

† Present address: Department of Chemical Engineering, Yonsei University, Seoul, 120- 749, South Korea.

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10.1021/ja0677057 CCC: $37.00

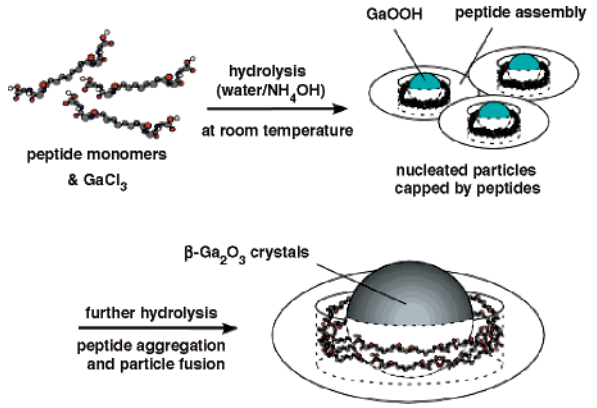

Figure 1. Illustration of β-Ga_2O_3 growth mechanism in the peptide capping assembly.

this biomimetic approach, the hydrolytic enzyme motif from the silicateins, consisting of nucleophilic hydroxyl of serine and amine of histidine, catalyzed the hydrolysis of the gallium precursors and resulted in both GaOOH and γ-Ga_2O_3 nanocrystal formation with a wide size range.[6] Although the synthesis of γ-Ga_2O_3 at room temperature was notable, the size and shape controls were hardly achieved, which could limit its industrial applications. Therefore, it is desirable to develop improved biomimetic templating systems with catalytic activities that can control the shape and the structure of semiconductor nanoparticles simultaneously.

Previously, we have discovered that the peptide assemblies templated and grew metal nanoparticles inside.[16] Recently, peptide assemblies also hydrolyzed $BaTi(O_2CC_7H_{15})[OCH(CH_3)_2]_5$ and produced ferroelectric tetragonal $BaTiO_3$ nanoparticles at room temperature.[17] Here, we report that the peptide assemblies from bolaamphiphile peptide monomers, bis(*N*-α-amidoglycylglycine)-1,7-heptanedicarboxylate, have chemical moieties catalyzing kinetically unfavored crystal growth of monodisperse β-Ga_2O_3 nanoparticles via aggregation-driven crystallization process (Figure 1). While the gallium precursors were hydrolyzed to GaOOH with base catalysts at room temperature, the gallium precursors were further hydrolyzed to β-Ga_2O_3 only when the peptide assemblies capped those particles. Unlike other growth methods, crystallization with the peptide assemblies could grow single-crystalline and monodisperse β-Ga_2O_3 nanoparticles selectively from gallium precursors in high yield. This unique feature of the uniform and selective crystal growth would be regulated by catalytic templating, fusion of nucleated particles, and nanoscale growth confinement in the peptide assemblies.

Experimental Section

Materials. The peptide assemblies were prepared by self-assembly of the bolaamphiphile peptide monomers, bis(*N*-α-amidoglycylglycine)-1,7-heptanedicarboxylate. Detailed protocol for the preparation of bolaamphiphile peptide monomer is described in previous reports.[18,19] The gallium precursor, gallium(III) chloride (anhydrous, 99.99%), and ammonia solutions (29.2% and 5.0 M, respectively) were obtained from Sigma−Aldrich and used as received.

Hydrolysis of Gallium Precursors in Peptide Assemblies. When 1 mL of bolaamphiphile peptide monomer solution (4.2 mg/mL) was mixed with 100 μL of $GaCl_3$ solution (10 mM) under nitrogen and then a volume of 200 μL of NH_4OH solution (15 M) was added to the above mixture to adjust its pH to 10.0, the gallium precursors were hydrolyzed to GaOOH capped with the peptide assemblies after 1 week. After 2 weeks of hydrolysis in the dark at room temperature, both GaOOH and β-Ga_2O_3 nanoparticles associated with the peptide assemblies were observed. After 3 weeks, all GaOOH nanoparticles were converted to β-Ga_2O_3 nanoparticles in the peptide assemblies in various particle sizes. After 4 weeks, all particles in the peptide assemblies were grown to β-Ga_2O_3 nanoparticles with diameter 50 nm. As a control experiment, the same hydrolysis of gallium precursor was examined at pH 7 by balancing acidity with 500 μL of citric acid (0.5 M), and only GaOOH nanocrystals were formed in this condition. Another control experiment was examined under the same experimental conditions without the peptide, and this condition also yielded only GaOOH particles.

Characterization. The shape and crystalline structures of synthesized nanocrystals were studied by transmission electron microscopy (TEM, JEOL model 1200EX, 100 ekV) and accompanying selected area electron diffraction (SAED). The SAED patterns were obtained at a camera distance of 12 or 60 cm. In the preparation of TEM specimens, a volume of 9 μL of the nanocrystal suspension was dropped on the formvar/carbon-coated copper grid and dried in air. No staining solution was applied to prevent artifacts.

Results and Discussion

After the bolaamphiphile peptide monomers were associated with the gallium precursors for 1 month at pH 10, β-Ga_2O_3 nanoparticles were synthesized and the TEM image is given in Figure 2a. This TEM image shows that those nanoparticles were grown to an average diameter of 50 nm with a narrow size distribution (Supporting Information), and their selected area electron diffraction (SAED) pattern (inset of Figure 2a) shows the single crystalline structure of monoclinic form of β-Ga_2O_3. This nanoparticle had an emission at 389 nm, consistent with photoluminescence (PL) of β-Ga_2O_3 nanoparticles (Supporting Information).[4] Magnified TEM images in Figure 2b show layers of peptides around the core particles. When the gallium precursor was hydrolyzed at the same experimental condition without the peptide, polydisperse particles in the diameters of 15−150 nm were observed as shown in Figure 2c, and their SAED shows that these particles were GaOOH (inset of Figure 2c). The base solution hydrolyzes gallium precursors to form GaOOH; however, it is not strong enough to drive the hydrolysis further to form β-Ga_2O_3 through condensation.[6] Therefore, these outcomes indicate that the peptides have the catalytic function to grow β-Ga_2O_3 nanoparticles at room temperature.

To understand the growth mechanism, the nanoparticle growth was monitored with TEM and SAED at different growth stages. After 1-week hydrolysis of gallium precursor with the peptide, small nanoparticles with diameter ~10 nm were observed with the capping peptide assemblies (Figure 2d). However, those particles were shown to be GaOOH from their SAED pattern. After 2 weeks of hydrolysis, both aggregated larger nanoparticles and smaller nanoparticles were observed in the peptide assemblies (Figure 2e). Some of the gallium nanoparticles fused with each other to form larger particles, indicated by arrows. Smaller particles were also incorporated in the aggregated peptide assemblies shown in the inset of Figure 2e. This fusion

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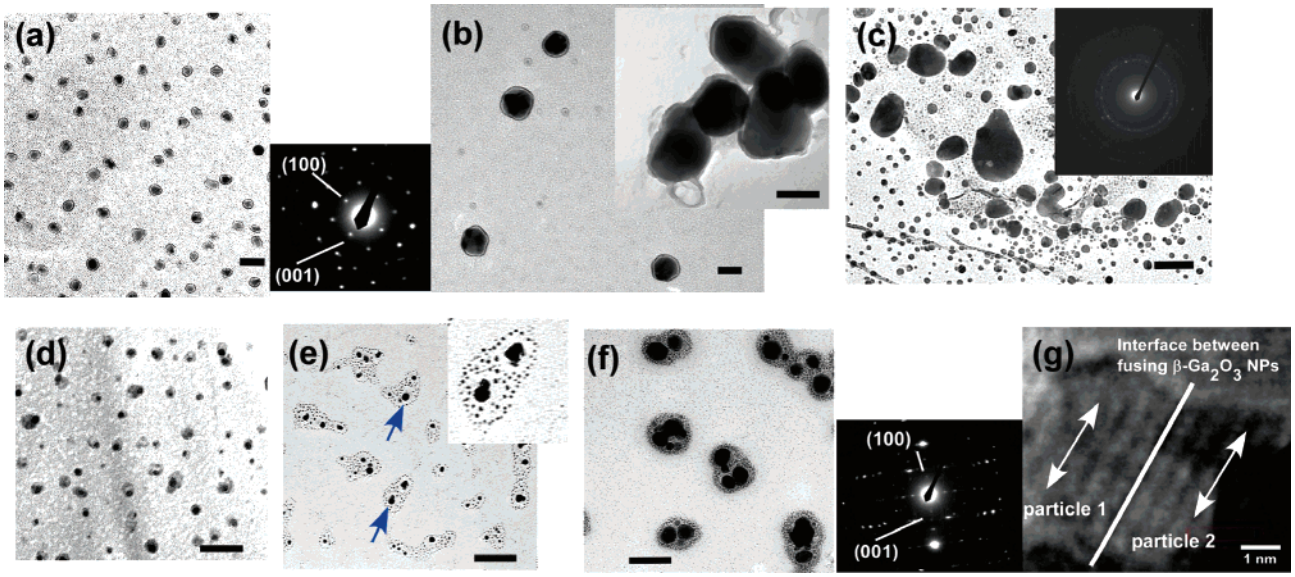

Figure 2. TEM image of β-Ga_2O_3 nanoparticles after 4 weeks of hydrolysis with the peptide: (a) low magnification, SAED pattern,sScale bar = 100 nm; (b) medium magnification (inset: high magnification), scale bar = 50 nm. (c) TEM image of GaOOH particles grown without the peptide and the SAED pattern. Scale bar = 80 nm. (d) TEM image of GaOOH nanoparticles grown after 1 week of hydrolysis with peptides. Scale bar = 20 nm. (e) TEM image of nanoparticles grown with the peptide after 2 weeks (inset: high magnification). Scale bar = 50 nm. (f) TEM image and SAED pattern of β-Ga_2O_3 nanoparticles after 3 weeks of hydrolysis with peptides. Scale bar = 50 nm. (g) HRTEM of fusing β-Ga_2O_3 nanoparticles. (200) lattice faces for both particles 1 and 2, shown by arrows, are aligned parallel to the particle-merging interface.

of particles inside the peptide assemblies proceeded further after 3 weeks, as shown in Figure 2f. Since those small particles and the fusing nanoparticles were not observed in the 4-week-old sample in Figure 2a and the size of Ga_2O_3 nanoparticles in the 4-week-old sample was larger than those in the 2-week-old sample, these results suggest that the small particles in Figure 2e,f fused with each other to grow larger Ga_2O_3 nanoparticles in the peptide assemblies. This type of nanoparticle fusion in capping agents to grow mesoscale crystals, aggregation-driven crystallization, was observed in various biomineralization processes in nature, and recently this process was mimicked to grow mesocrystals in organic media by fusing primary nanoparticle-building blocks in aggregated micelles and capping polymers.[20−22] In the same fashion, it is plausible that the highly crystalline β-Ga_2O_3 particles of diameter 50 nm were formed by the fusion of small particles in the capping peptide assemblies. To obtain a better understanding of the particle-fusion mechanism, the SAED patterns of nanoparticles at different growth stages were compared. The SAED of fusing nanoparticles in the 3-week-old sample (Figure 2f) shows the faint and fused (100) and (001) spots. This pattern indicates that those particles preferentially oriented to their [010] crystallographic direction and their [100] and [001] directions were not aligned well.[23] SAED of the fused nanoparticles in the 4-week-old sample (Figure 2a) shows the strong intensities of the (100) and the (001) spots with the single crystalline structure. These SAED patterns indicate that the nanoparticles in Figure 2f were aggregated along the [010] direction to grow single-crystalline β-Ga_2O_3 particles shown in Figure 2a.[23] High-resolution (HR) TEM of fusing β-Ga_2O_3 nanoparticles at the particle-merging interface also supports this growth mechanism. As shown in Figure 2g, the (200) lattice fringe of the particle 1 was parallel to the (200) lattice fringe of the particle 2 around the merging area. This HRTEM image indicates that β-Ga_2O_3 nanoparticles are fused to the preferential orientation of their [010] crystal direction, consistent with the SAED results.

Because β-Ga_2O_3 nanoparticles were observed in the presence of peptide after 2 weeks of hydrolysis and only GaOOH particles were obtained in the same experimental conditions without the peptide, the peptide assemblies must have a catalytic activity in the hydrolysis reaction of gallium precursors. On the basis of the study on proteins of glassy skeletal spicules in marine sponge, silicateins, it has been shown that chemical moieties of nucleophilic hydroxyl groups of serine catalyzed hydrolysis reactions when they were hydrogen-bonded with amine groups of the neighboring histidine.[6] Similarly, the carboxyl group in the peptide assemblies could also catalyze the hydrolysis as they are hydrogen-bonded with the neighboring amine. Although the carboxyl moiety is a weaker hydrolysis agent compared to hydroxyl,[24] hydrogen bonding with the amine could amplify nucleophilicity of the carboxyl group to strengthen the catalytic activity of the hydrolysis, as observed in the silicatein. To probe the complexation among the carboxyl, the amine, and gallium ions, Fourier transform infrared (FT-IR) spectroscopy was applied. The FT-IR spectrum of the gallium−peptide complexes (black line in Figure 3) shows characteristic symmetric COO^-, asymmetric COO^-, and NH_2^+ bands of the bridged metal complex, COO^-−Ga−NH_2^+ at 1423, 1563, and 1620 cm^{-1}, respectively, in addition to peaks originated from the peptide assemblies.[25,26] This observation supports our hypothesis that

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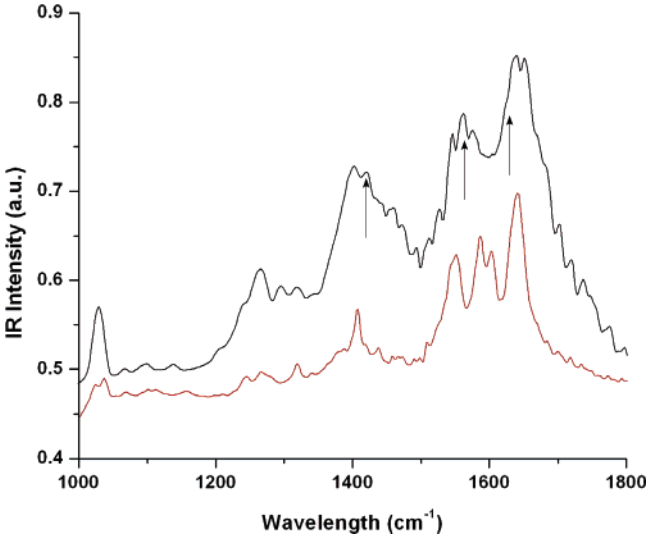

Figure 3. FTIR spectra of neat peptides (red) and peptides complexed with the gallium ions (black). Arrows show peaks corresponding to vibrations of COOH and NH_2 complexing with gallium ions.

the gallium hydrolysis took place at the juxtaposition of the carboxyl and amine moieties in the peptide assembly.

To confirm our hypothesis that the hydrolysis is catalyzed by hydrogen-bonded carboxyl groups of the peptide, we examined a control experiment to weaken the strength of hydrogen bonds between the carboxyl and amine groups during the growth process. When the gallium precursor was hydrolyzed at pH 7, the protonated carboxyl group bound the amine group more weakly, and the weaker nucleophilicity of the carboxyl reduced the degree of gallium hydrolysis. Under this condition, after the hydrolysis of the gallium precursor with the peptide for 4 weeks, only GaOOH crystals were observed in the peptide assemblies due to the lack of strong hydrolysis activity (Figure 4a). This result is consistent with our hypothesis that the chemical moieties of hydrogen-bonded carboxyl and amine catalyze the hydrolysis of gallium precursors to form β-Ga_2O_3 crystals.

In addition to the influence of chemical moieties of peptide for the catalytic activity, the shape and dimension of capping peptide assembly could also promote gallium hydrolysis. Previously, the dehydration of calcium carbonate was accelerated in porous templates because those pores functioned as pathways for water exclusion and dehydration.[7] The pores of the peptide assemblies capping nanoparticles could also provide a dehydration pathway promoting β-Ga_2O_3 growth in the cavities. Another potential factor to contribute to β-Ga_2O_3 crystallization in the peptide assembly is the high surface tension built in the nanoscale peptide cavities. Previously, when mineralization of calcite occurred in micrometer-scale pores of membranes, the resulting crystals in the pores were observed to have unusual crystalline structures due to high surface tensions in such small confinements that altered the reaction kinetics of crystal growth.[27] We believe that the peptide templates could also exploit this strategy of the confinement-controlled mineralization one step further to nanoscale, and the confinement effect of the peptide assemblies could assist the unusual β-Ga_2O_3 crystallization at room temperature.

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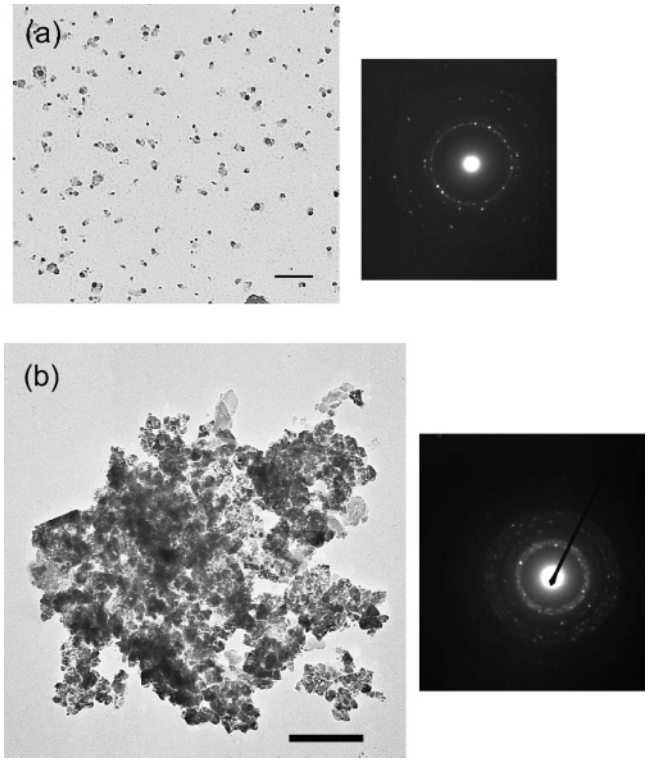

Figure 4. TEM images and electron diffractions: (a) GaOOH particles obtained after 4 weeks of hydrolysis with the peptide at neutral pH, scale bar = 100 nm; (b) GaN particles obtained after the sintering of Ga_2O_3 nanoparticles under NH_3 at 900 °C, scale bar = 200 nm.

When these nanoparticles were sintered at 900 °C under NH_3, the peptide assemblies were removed and the oxide particles were transformed to GaN (Figure 4b). Through the sintering process, the peptide assemblies were removed. The baked GaN nanoparticles were aggregated, and this aggregation is probably due to the high surface energy of uncapped nanoparticles and the sample drying effect.

Conclusions

Peptide assemblies were applied as catalytic nanoreactors to grow β-Ga_2O_3 at room temperature. This peptide assembly template accompanied with the enzymatic functionality catalyzed the hydrolysis of gallium precursors. While the conventional base catalyst hydrolyzed the gallium precursors to GaOOH, the peptide assembly could further promote the reaction to crystallize β-Ga_2O_3. Due to the catalytic chemical moieties of the peptide, the kinetically unfavored β-Ga_2O_3 crystal growth was achieved in ambient conditions when the nucleated particles were capped by the peptide assemblies. In addition to the enzymatic chemical moieties of the peptide assembly, the nanoscale cavity created by capping particles could provide both the efficient dehydration pathway and the optimal surface tension control, which are advantageous for β-Ga_2O_3 crystal growth. This multifunctional peptide assembly is expected to be applied for the syntheses of a variety of nanomaterials that are kinetically difficult to grow at room temperature.

Acknowledgment. This work was supported by the U.S. Department of Energy (DE-FG-02-01ER45935) and partially supported by the National Institute of Health (2S-06-GM60654-

06). Hunter College infrastructure is supported by the National Institutes of Health, the RCMI program (G12-RR-03037). S.-Y.L. thanks Professor C. Rojo and Dr. J. Carvajal for use of the electrical furnace in the Department of Materials Science at State University of New York, Stony Brook. We also thank Professor K. Fath and Dr. A. Tsiola at Core Facilities for Imaging, Cellular and Molecular Biology at Queens College, City University of New York, for use of the transmission electron microscope.

Supporting Information Available: Size distribution of β-Ga_2O_3 nanoparticles, AFM image of β-Ga_2O_3 nanoparticles, and PL spectrum of β-Ga_2O_3. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0677057