Polycrystalline nanowires of gadolinium-doped ceria via random alignment mediated by supercritical carbon dioxide

Sang Woo Kim & Jae-Pyoung Ahn

1Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea, 2Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea.

This study proposes a seed/template-free method that affords high-purity semiconducting nanowires from nanoclusters, which act as basic building blocks for nanomaterials, under supercritical CO2 fluid. Polycrystalline nanowires of Gd-doped ceria (Gd-CeO2) were formed by CO2-mediated non-oriented attachment of the nanoclusters resulting from the dissociation of single-crystalline aggregates. The unique formation mechanism underlying this morphological transition may be exploited for the facile growth of high-purity polycrystalline nanowires.

Results

Morphological evolution of Gd-CeO2 nanomaterials. The P-T map in Fig. 1, which is experimentally classified by SEM and TEM observations, can be divided into three distinct regions—Regions 1, 2, and 3—corresponding to the morphology of the synthesized Gd-CeO2 nanomaterials on the basis of temperature and pressure. The SEM and TEM images corresponding to each region (Figs. 2a–d) revealed the morphological evolution from nanoclusters (Region 1) to nanowires (Region 3) via the formation of aggregates (diameter: ~250 nm) (Region 2). The nanoclusters formed in Region 1 were spherical and monodisperse, and their size and shape remained unchanged even at higher pressures and temperatures (see supplementary Figure S1 for more details).
The nanoclusters formed in Regions 2 and 3 assembled into spherical aggregates that then transformed into nanowire bundles, as shown in Fig. 2c.

Formation of nanoclusters and aggregates. Figure 3 shows TEM images of the Gd-CeO$_2$ nanoclusters and single-crystalline aggregates observed in Regions 1 and 2, including the selected-area diffraction (SAD) pattern and fast Fourier transform (FFT) patterns in the inset. The nanoclusters include a stable Gd-CeO$_2$ phase with a face-centred cubic fluorite structure (average size: 3 nm), as indicated by the dotted circles in Fig. 3a, and are highly crystalline, as indicated by the sharp ring pattern in the inset of Fig. 3a. The HRTEM images and FFT patterns in Fig. 3b indicate that individual nanoclusters comprise a single-crystalline Gd-CeO$_2$ phase. TEM and HRTEM images (Fig. 3c–f) acquired from specific regions on each aggregate revealed that the aggregates have many nanosized terraces at their surfaces. Although the aggregates comprised single-crystalline CeO$_2$, they were loosely packed as evidenced by the broad spots in the FFT patterns (inset of Figs. 3d, f). A unique contrast indicative of a 3-nm cluster was observed in the HRTEM images (indicated by dotted circles in Fig. 3d), strongly suggesting that the growth of seed-free single-crystalline aggregates in the supercritical fluid is preceded by the coalescence of the precursors (Fig. 8a) underwent collision and coalescence in the supercritical fluid to yield aggregates with intercluster interfaces. The nanoclusters formed by dissolution and precipitation of the precursors (Fig. 8a) underwent collision and coalescence in the supercritical fluid to yield aggregates with intercluster interfaces. The nanoclusters in the aggregates aligned themselves into a single crystal such that the interfacial diffusion of the CO$_2$ molecules (diameter: 3.87 Å) to diffuse into the cluster lattice (largest (111) d-spacing of CeO$_2$: 3. 12 Å). Thus, HRTEM observations of the aggregate surfaces strongly evidenced the dissociation-driven morphological transition from aggregates to nanowires between Regions 2 and 3 in the P-T map.

Random growth of polycrystalline nanowires. At high temperatures and pressures, efficient CO$_2$ permeance into the aggregates led to the formation of nanowire bundles (Fig. 5). Nanowires were present inside the aggregates separated into individual nanowire bundles (Fig. 7). Random growth of polycrystalline nanowires comprises single-crystalline nanoclusters without any specific growth direction could be seen at the aggregate/nanowire sprout junction (Figs. 6b, c). However, the region marked by rectangle d in Fig. 6a (magnified image shown in Fig. 6d) revealed the original single-crystal structure. The complete transformation of all single-crystalline aggregates to polycrystalline nanowire bundles (Fig. 7) clearly implied that this unusual growth process is attributable to the dissociation and reconstruction of nanoclusters. The nanowire bundles were well separated into individual nanowires (diameter: ~20 nm; length: ~10 μm) by ultrasonic impact. The nanowire bundles (Figs. 7b, c) comprised several polycrystalline nanowires, each of which included randomly aligned nanoclusters that serve as the building blocks for nanowire assembly.

Discussion

Figure 8 schematically summarizes the mechanism underlying the unique nanoparticle-to-polycrystalline-nanowire transition (see Supplementary Movie 1). While the formation mechanisms for nanoclusters and single-crystalline aggregates were similar to those reported previously, the mechanism of polycrystalline nanowire growth beyond Region 2 was different. The nanoclusters formed by dissolution and precipitation of the precursors (Fig. 8a) underwent collision and coalescence in the supercritical fluid to yield aggregates with intercluster interfaces. The nanoclusters in the aggregates aligned themselves into a single crystal such that the interface...
energy was minimized, and they eventually formed a loosely packed structure (similar to a mosaic structure, Region 2 in Fig. 8b).

In the transition region and Region 3, the balance between the interfacial energy of the nanoclusters in the aggregates and the permeance of CO$_2$ should be considered. The interfacial energy decreases markedly with an increase in pressure and temperature because the liquid/solid interfacial tension becomes almost zero under the supercritical conditions. Thus, the penetrating force is more dominant than the interfacial energy. As a result, the single-crystalline aggregates dissociate into nanoclusters (Fig. 8c) and reassemble to form polycrystalline nanowires inside and outside the aggregates (Figs. 8d, e). While the formation of polycrystalline nanowires by the random alignment of nanoclusters in the absence of functional capping agents and catalyst seeds leading to self-aligned growth of nanowires is established, it is difficult to provide a thermodynamic explanation for the growth mechanism (see Figure S2 for the kinetic details controlled with time). The random orientation of the polycrystalline nanowires implies non-selective attachment of CO$_2$ molecules on arbitrary crystal planes of the nanoclusters in the metastable transition region. The fusion of the uncapped regions of the nanoclusters is energetically favourable as this reduces the difference in surface energy between the nanoclusters and facilitates the formation of polycrystalline nanowires (Fig. 8f). Thus, supercritical CO$_2$ is confirmed to be the appropriate medium for the growth of polycrystalline nanowires.

In summary, the formation of Gd-CeO$_2$ nanomaterials such as nanoclusters, aggregates, and nanowires in a supercritical CO$_2$-ethanol system was analysed on the basis of a P-T map divided into...
three regions. The single-crystalline aggregates comprised loosely aligned nanoclusters for minimizing the high interfacial energy between the nanoclusters under low CO₂ permeance. In the transition region with higher CO₂ permeance, the aggregates dissociated into nanoclusters partially covered by CO₂, which in turn attached to one another non-selectively to afford polycrystalline nanoclusters. This type of reconstruction is significant in that it opens up a new nanowire fabrication route without the need for seeds or capping agents, facilitates large-scale production, and could be applied to other materials.

**Methods**

**Synthesis of Gd-CeO₂ nanomaterials.** For solvothermal crystallization using supercritical carbon dioxide, 65 mL ethanolic solutions of cerium nitrate Ce(NO₃)₃·6H₂O with 99% purity, including 20 mol% gadolinium nitrate Gd(NO₃)₃·6H₂O (concentration: 45–90 mg/mL), were fed to a 350-mL high-pressure vessel. The vessel was charged with 99.99% CO₂ at pressures of up to 7.5 MPa at 35 °C and then heated for 15 min at 100–140 °C and 5–35 MPa until the ethanolic solution and CO₂ reached the supercritical fluid state. Subsequently, the reaction solution was cooled to ambient temperature without water cooling, and then, the vessel was slowly depressurized for 10 min. The as-synthesized nanomaterials were collected by sedimentation, centrifuged at 1,400 rpm for 10 min in a 3,000 rpm) for 10 min in a 15-mL conical centrifuge tube, repeatedly washed with ethanol three times, and dried at 60 °C for 12 h.

**Microstructural characterization.** The morphology and microstructure of the nanomaterials were examined by scanning electron microscopy (SEM, Nova NanoSEM, FEI, USA) and transmission electron microscopy (TEM, Tecnai F20, FEI, USA) as well as high-resolution TEM (HR-TEM) and energy-dispersive X-ray spectrometry (EDS, EDAX). Cryo-TEM was adopted to investigate the actual dissociation state of the aggregates. In this method, the nanomaterial solution exiting the fluid chamber was cooled to cryogenic temperatures by the Vitrobot, and a 100-nm-thick vitrified film indicative of the near in situ state during the dissociation reaction was prepared.

For observing the dissociation behaviour of aggregates, in particular, we prepared the ex-situ TEM sample by putting C-coated TEM grids on the glass positioned at the centre region of the chamber.

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**Author contributions**

S.W. and J.P. contributed equally to this work by conceiving and discussing the project.

**Additional information**

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