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Organic-Ligand-Assisted Hydrothermal Synthesis of Rare Earth Doped Ceria Nanocubes[†]

YAMAMOTO Kazuhiro*, HASHISHIN Takeshi*, QIU Nan*, TAN Zhenquan*, OHARA Satoshi**

Abstract

Ceria and Gd-doped Ceria (GDC) nanocubes covered with highly reactive {001} facets were synthesized via organic-ligand-assisted hydrothermal treatment with water soluble amino acid 6–amino hexanoic acid (AHA). The particle shape and size were much controlled and these nanocube materials were easily dispersed in water and alcohol solvent. It can be noted that the coordinate of AHA had hydrophilic groups and short methylene chains.

KEY WORDS: (Hydrothermal synthesis), (organic ligand), (nanoparticles), (nanocubes), (SOFCs)

1. Introduction

Cerium oxide materials have attracted much attention as high performance anode material for low-temperature solid-oxide fuel cells (SOFC) in recent years. Rare earth doped ceria, especially gadolinium doped ceria (GDC) is considered to be one of the most promising materials for operating at a temperature below 600 °C. Morphology control of the anode materials by a solution method has reported,^{1,2)} though the controlled morphologies, particle shape and size disappeared after sintering at a temperature over 1300 °C. Therefore, many researchers apply simple ball milling for grinding and mixing of NiO and GDC powders, and focus on only control of the microstructure.^{3,4)} High temperature sintering at 1300 °C is needed for forming of the NiO and GDC framework, though which drastically decreases the triple-phase boundary (TPB) as a reaction site of hydrogen gas and oxygen ion as a result of coarsening of NiO and GDC.

Recently, Zhang et al. have reported supercritical hydrothermal synthesis of tailor-made ceramic nanocrystals with organic ligands selectively adsorbed on particular crystal planes.⁴⁻⁷⁾ In their studies, ceria

nanocubes with highly reactive {001} crystal facets⁸⁾ were synthesized by supercritical hydrothermal treatment with a carboxylic acid such as decanoic acid ($\text{CH}_3(\text{CH}_2)_8\text{COOH}$) and hexanoic acid ($\text{CH}_3(\text{CH}_2)_4\text{COOH}$). The {001} facets participated in the extra-low-temperature oxygen storage capacity. Such a novel singular functional material is expected to contribute to the lowering of the working temperature because of the enlarged TPB caused by low-temperature anode sintering owing to the high energy crystal surface.

In Zhang's study, hydrophobic decanoic acid and hexanoic acid were used as organic ligands to induce {001} crystal facets. Accordingly, the ceria nanocubes can be disperse in non-polar solvent such as toluene and hexane because of coordination of organic ligands having long methylene chains. Water is a most useful green solvent owing to the safety, low cost and abundant resources; therefore, we examined controlling of the surface condition induced by water-soluble organic ligands. We focused water-soluble amino acid 6–amino hexanoic acid ($\text{H}_2\text{N}(\text{CH}_2)_4\text{COOH}$: AHA) for the control of crystal facets and the development of hydrophilicity. In our

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study, we report organic-ligand-assisted hydrothermal synthesis of rare earth doped ceria nanocubes with AHA and control of the particle shape, size, crystal plane and surface condition.

2. Experimental

All reagents were used as received without further purification. $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) nanocubes were synthesized by organic-ligand-assisted hydrothermal treatment. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2.7 mmol, Wako Pure Chemical), $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.3 mmol, Kanto Chemical), and AHA (18 mmol, Tokyo Chemical Industry) were dissolved in distilled water (29.5 mL). In addition, *tert*-butylamine (0.5 mL, Tokyo Chemical Industry) was quickly added to the mixed solution with vigorous stirring at room temperature. After 5 min of stirring, the mixture became a light purple transparent sol precursor, which was placed in a Teflon-lined stainless steel autoclave (total volume was 50 mL), where it was then heated at 180 °C for 24 h for the growth of {001} facets with coordination of AHA. The GDC nanocube precipitate was isolated by centrifuging and then washed three times with distilled water.

3. Results and discussion

Fig. 1 shows XRD patterns of ceria samples synthesized by organic-ligand-assisted hydrothermal treatment heated at 180 °C for 24 h with AHA. All samples showed diffraction patterns containing characteristic diffraction peaks corresponding to CeO_2 (CaF_2 structure), and the diffraction peaks were also observed to shift to higher angles with increasing Gd concentration. Thus, it was confirmed that there was no formation of a secondary phase in the samples.

The particle morphologies of ceria and GDC samples were characterized by TEM observation. As shown in **Fig. 2(a)** and (b), the particle sizes of

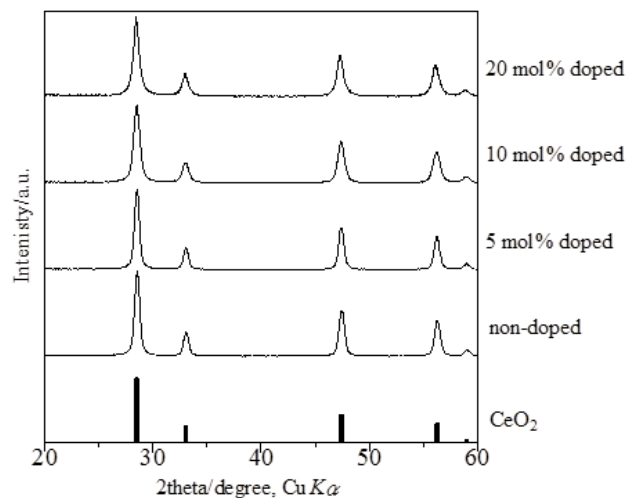


Fig. 1 XRD patterns of samples prepared by organic-ligand-assisted hydrothermal method heated at 180 °C for 24 h with AHA.

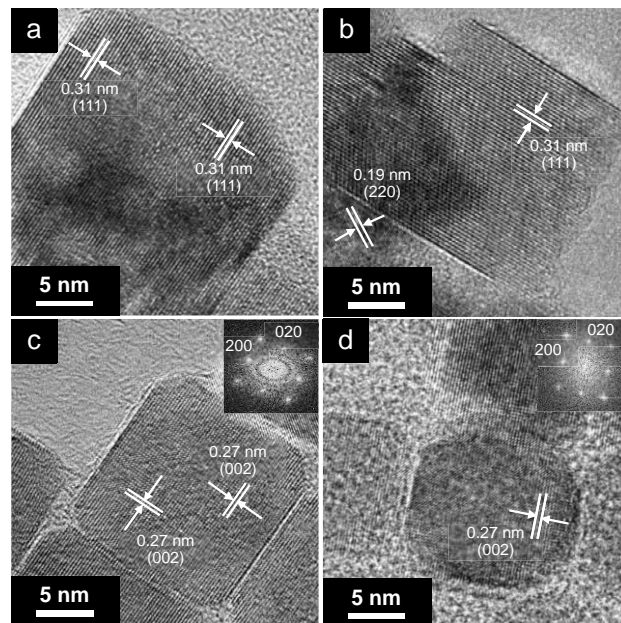


Fig. 2 HR-TEM images of ceria sample (a) without AHA and non Gd doped, (b) without AHA and 10 mol% Gd doped, (c) with AHA and non Gd doped, (d) with AHA and 10 mol% Gd doped.

conventional ceria and GDC samples were approximately 25 and 20 nm respectively, and only 0.31 and 0.19-nm lattice fringes corresponding to the (111) and (220) facets were confirmed. **Fig. 2(c)** and (d) show particle morphologies of ceria and GDC samples prepared by organic-ligand-assisted hydrothermal treatment. The particle sizes were about 15 and 10 nm, and 0.27-nm lattice fringes corresponding to the (002) facets were observed, furthermore, which were confirmed to have cubic morphology. Therefore, ceria and GDC nanocubes covered with highly reactive {001} facets were successfully obtained by organic-ligand-assisted hydrothermal treatment. The inset fast Fourier transform (FFT) image shows {002} diffractions, which also supported the results. Ceria and GDC nanocube had smaller particle sizes compared with conventional ceria and GDC nanoparticles, which indicated that the AHA molecule played a part in controlling the particle shape and size under hydrothermal conditions.

AHA coordination on the {001} crystal facets of ceria and GDC nanocubes was identified by FT-IR spectroscopy measurements. As shown in **Fig. 3**, the 2927 and 2856 cm^{-1} bands and the 1433 cm^{-1} band in the spectra, corresponding to C–H stretching of the methylene chain and the stretching frequency of the carboxylate group, respectively, indicated that the carboxylate group in AHA was chemically bonded to Ce ions on the {001} facets.^{9,10} On the other hand, the ceria and GDC nanocubes were easily dispersed in water, methanol, and ethanol owing to coordination of

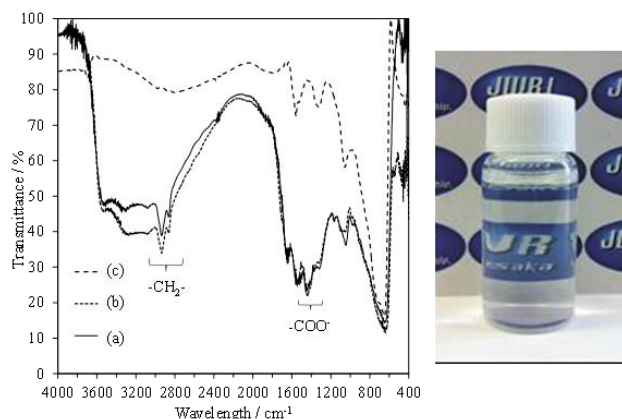


Fig. 3 Left: FT-IR spectra of cerium oxide samples: a) CeO_2 reagent (Wako Pure Chemical); b) CeO_2 nanocubes; c) GDC nanocubes. Right: Photograph of GDC nanocube suspension in water.

AHA with short methylene chains and the terminal hydrophilic amino group. AHA ($\text{H}_2\text{N}(\text{CH}_2)_4\text{COOH}$) and hexanoic acid ($\text{CH}_3(\text{CH}_2)_4\text{COOH}$) have similar structures, though ceria nanocubes coordinated with hexanoic acid cannot be dispersed in water due to their low solubility in water. Therefore, water dispersibility of ceria and GDC nanocubes coordinated with AHA is obviously attributed to the hydrophilicity of amino group. Therefore, these results indicate that it is important to design the structure of the organic ligand for controlling surface condition. In the photograph of Fig. 3, GDC nanocube suspension shows very high transparency in water solvent.

4. Conclusions

Highly reactive $\{001\}$ crystal facets and cubic morphology were successfully induced in ceria and GDC nanoparticles by the organic-ligand-assisted hydrothermal method with water-soluble amino acid 6-amino hexanoic acid, and Gd doping was confirmed from the diffraction peak shifts to higher angles with increasing Gd concentration. Controlling of the particle shape, size, crystal plane and surface condition were achieved by coordination of 6-amino hexanoic acid.

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