Supporting Information

Nanoscale Heterogeneities in CeO_2-ZrO_2 Nanocrystals Highlighted by UV-Resonance Raman Spectroscopy

Takaaki Taniguchi, Tomoaki Watanebe, Satoshi Ichinohe, Kenichi Katsumata, Masahiro Yoshimura, Kiyoshi Okada, and Nobuhiro Matsushita

S1. Experimental Section

S1-1. Synthesis. A total amount of 3.5 mmol of $(NH_4)_2Ce(NO_3)_6$ (Aldrich, 98.5%) and $ZrOCl_2 \cdot 8H_2O$ (Wako, 99.5%) in the molar ratio Zr/(Ce+Zr) = 0, 80, or 50%, was dissolved in distilled water (30 mL) at room temperature. Subsequently, we added ammonia (5 mL, 25 wt% aqueous solution, analytical grade, Wako) to the solution mixture. Then, the reaction mixture was placed in a polytetrafluoroethylene vessel (40 cm^3 inner volume). The vessel was sealed and placed inside a stainless steel autoclave, which remained at 200°C for 6 h under autogenous pressure. The products were collected by centrifugation (5000 rpm for 30 min), washed twice with distilled water, and then dried at 80°C for 6 h in air. Finally, we calcined the products at 800°C. The

treatment involved heating for 2 h up to the final temperature and isothermal annealing for 5 h.

S1-2. Characterizations. We characterized the crystalline products by XRD spectroscopy with a Rigaku RINT 2000 diffractometer with Ni-filtered Cu-Kα radiation (λ = 1.54178 Å). The average crystallite sizes were calculated with the Debye–Scherrer formula using the line broadening of a (220) refraction of the cubic phase. Visible- and UV-Raman spectroscopy were carried out on a Jobin–Yvon T64000 spectrometer (resolution of 1 cm) using a visible laser (λ = 514.5 nm) and UV laser (λ = 363.8 nm) with a laser power output of 50 mW at room temperature. The scattered light was collected with backscattering geometry using a liquid nitrogen cooled charge-coupled device (CCD) detector. The measurement system for UV-Raman spectra, which was designed by our research group, is described in detail in Ref. 1. We performed UV-Vis diffuse-reflectance spectroscopy using a Perkin Elmer lambda 35 UV-Vis spectrometer to obtain the absorption spectra. Transmission electron microscopy (TEM) observation was performed using a Hitachi HF-2000 transmission electron microscope operating at 200 kV.

Ref. 1. Yashima, M.; Kakihana, M.; Shimidzu, R.; Fujimori, H.; Yoshimura, M., *Appl. Spectroscopy* **1997,** *51*, 1224.