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Improved Low-Temperature Reducibility in Ceria Zirconia Nanoparticles by Redox Treatments

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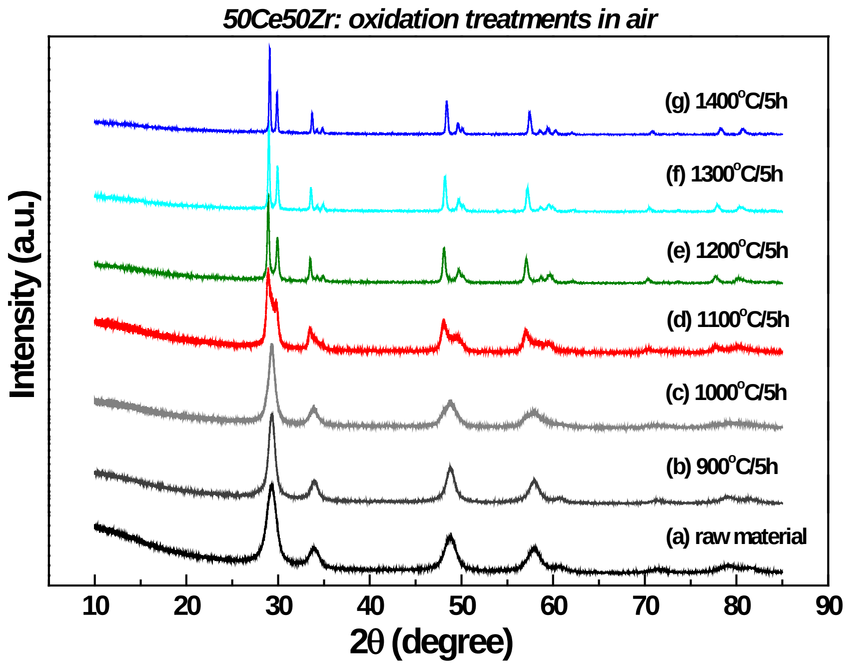
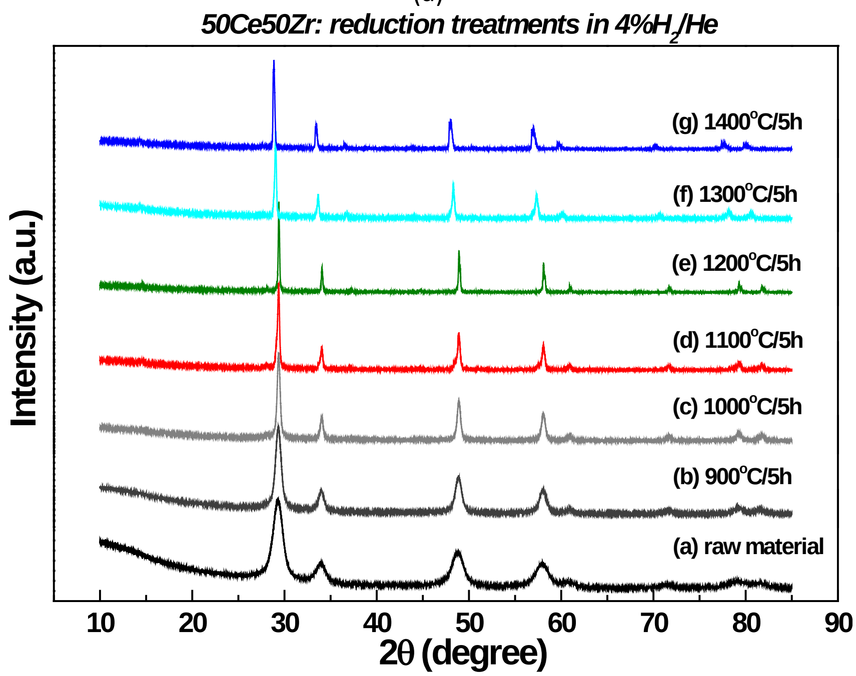
EXPERIMENTAL SECTION

Sample preparation and macroscopic reducibility: High-surface-area ceria zirconia samples were prepared using a spray freezing method and characterized with X-ray diffraction (XRD) for average structure and particle size, and thermalgravimetric analysis (TGA) for reducibility characterization (determination of reduction temperature and reduction percentage). For each redox cycle, the high-temperature reduction treatment was carried out in a TA Instruments 2050 TGA system at 1000^{o}C for about 3 hrs with the carrier-gas of 4%H_2/96%He mixture, and then the sample was transferred to a box furnace and reoxidized at different temperatures for 2hs in air. The mass loss is used to calculate the reduction percentage. The negative of the differential mass loss (derivative thermogravimetric profile, DTG) with respect to temperature (-dM/dT) is plotted with respect to temperature. The peaks in the DTG profiles correspond to the significant mass loss during reduction. The primary peak center in the DTG profiles is defined as the reduction temperature, where the maximum reduction rate occurs.

TEM characterization: High resolution transmission electron microscopy (HRTEM) and high-angle annual dark field scanning transmission electron microscopy image (HAADF-STEM, also called Z-contrast) were carried out to identify structural changes for the individual nanoparticles before and after redox treatment using JEOL 2100 TEM. For the electron energy loss spectroscopy (EELS) analysis, we used the $CeM_{4,5}$ integrated white line at 883 and 901 eV to determine the Ce oxidation state in individual nanoparticles. To avoid the electron beam damage, weak-beam technique with wide spread beam and selected area aperture were used to get the EELS spectra from individual nanoparticles in diffraction mode. Isolated nanoparticles hanging in the vacuum without overlap were selected for EELS analysis.

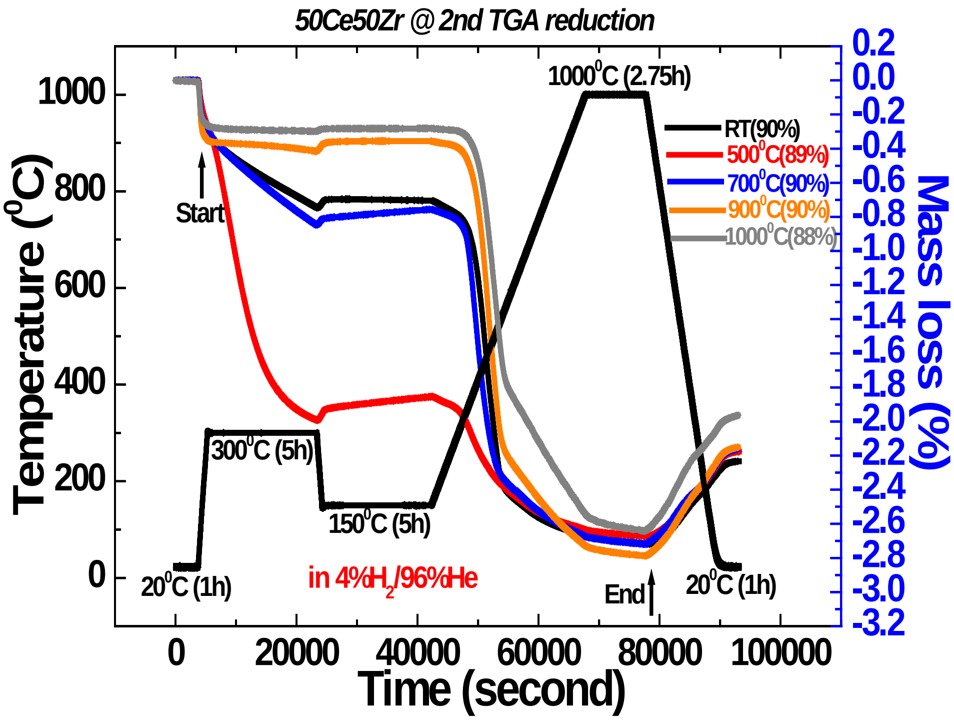


(a)

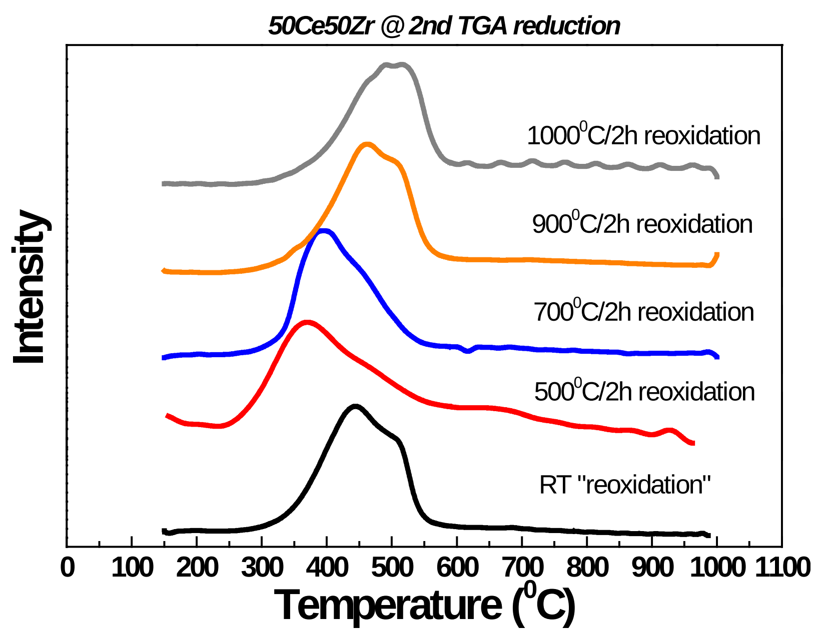


(b)

S 1. Effects of increasing thermal treatment temperature on the phase homogeneity of $Ce_{0.5}Zr_{0.5}O_2$ samples under oxidizing (a) and reducing atmosphere (b): (a) raw material; (b) 900 ^{o}C; (c) 1000 ^{o}C; (d) 1100 ^{o}C; (e) 1200 ^{o}C; (f) 1300 ^{o}C; (g) 1400 ^{o}C.



(a)



(b)

S 2. the thermogravimetric analysis (TGA) reduction (a) and derivative thermogravimetric (DTG) (b) profiles for the ceria zirconia sample during the 2nd reduction after a reoxidation treatment at different temperature from room temperature to 1000 ^{o}C, showing the effect of reoxidation temperature on the reducibility of the materials.