Supplementary Information

Figure S1 shows the XRD patterns and the laser Raman microspectra of the dried nanoparticles. The XRD data show that all of the peaks can be indexed according to the cubic fluorite structure of CeO_2 (ICSD 28709), the peaks are relatively wide, and there is no apparent preferred orientation. The width of the peaks suggests that the grains are poorly crystallized and/or they consist of very small crystallites.[1] TEM examination reveals that the nanoctahedra and nanorods exhibit relatively well formed but agglomerated morphologies as well as sharp electron diffraction patterns. The crystallite size was calculated using the Scherrer equation,[2] which assumes an isotropic grain shape (albeit with a limit of reliability of 1-2 nm). The calculated value of ~4 nm is of the same order of magnitude as that observed for the nanoctahedra cross-section of ~10 nm and for typical nanorods (4-5 nm width; aspect ratio ≤6). These data suggest why no preferred orientation of the nanorods was observed.

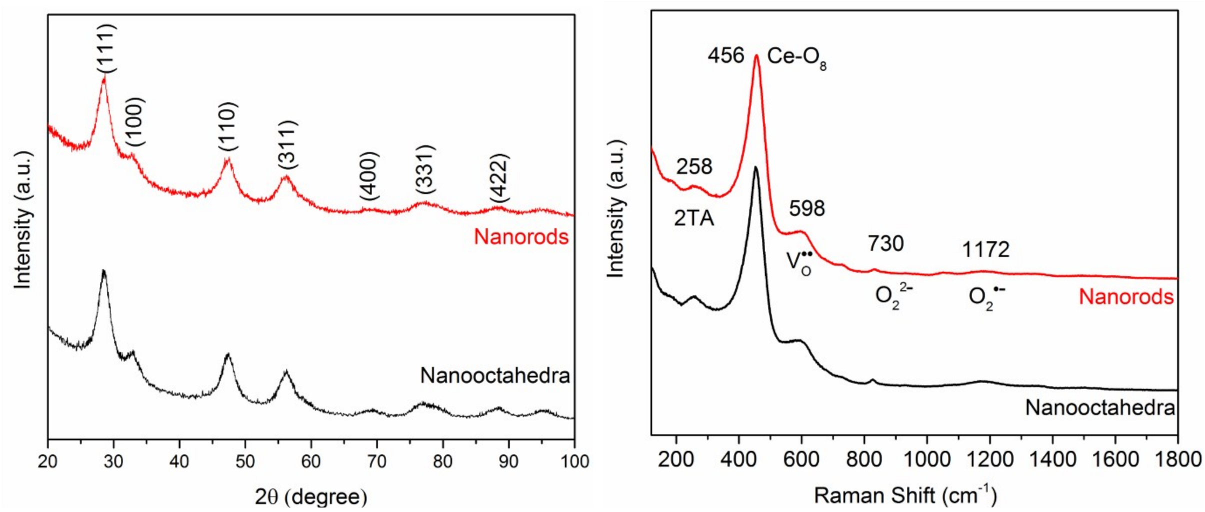

Figure S1. XRD patterns and laser Raman microspectra of the dried CeO_2 nanoparticles.

The dominant Raman signal at 456 cm^{-1} is attributed to the F_{2g} mode of CeO_2, which originates from the $Ce\text{-}O_8$ fundamental vibrational unit.[3] This vibrational mode softens (*i.e.*, peak broadening and decreasing intensity) in nanocrystalline CeO_2 and is a consequence of *phonon confinement*,[4] which reflects the proportional effect of crystallite size on the vibrational intensity. Typically, the F_{2g} mode of microceria vibrates at a frequency of 465 cm^{-1},[5] which is higher than the observed 456 cm^{-1} for the nanoceria of the present work. This red shift may derive from the following reasons:

1. When the crystallite size reaches nanoscale dimensions, the phonon selection rule (where the wavevector $k = 0$) no longer is valid. Consequently, phonon vibration across the entire Brillouin zone contributes to the Raman scattering, thereby resulting in a red shift.[6-8]
2. When the concentration of oxygen vacancy defects increases, this disrupts the vibration of the Ce-O_8, thereby resulting in a red shift.[9, 10]

In addition to the strongest peak, there are four peaks at 258, 598, 730, and 1172 cm^{-1}. According to the oxygen adsorption study by Wu *et al.*,[7] the weak mode at 258 cm^{-1} corresponds to the second-order transverse acoustic mode (2TA), the more intense mode at 598 cm^{-1} is due to the intrinsic defect-induced ($V_O^{\bullet\bullet}$) longitudinal optical mode (LO), also known as the D-band, the peak at 730 cm^{-1} results from the formation of superoxide (O_2^{2-}) species on the surface, and the broad bump at 1172 cm^{-1} is the second overtone band, which represents the doubly degenerate longitudinal optical mode (2LO). This latter mode is associated with the O–O stretching vibration mode of surface adsorbed superoxide anions ($^{\bullet}O_2^{-}$).[11] This superoxide radical is formed by the interaction of the surface-adsorbed oxygen with electrons trapped at oxygen vacancies.

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