## **Supporting Information**

## Sol-gel-derived ceria nanoarchitectures: Synthesis, characterization and electrical properties

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**X-ray diffraction:** We performed X-ray diffraction to assess the crystallinity of the as-prepared materials. Powder X-ray diffraction data were collected at room temperature (Bruker D8 Advance X-ray diffractometer) with CuK $\alpha$  radiation in the Bragg–Brentano geometry. These experiments show that the as-prepared material is amorphous for all three nanoarchitectures studied: aerogel, ambigel, and xerogel (Figure S1).



Figure S1. Powder X-ray diffraction patterns (background corrected) of as-prepared  $CeO_x$  nanoarchitectures: **a**. aerogel; **b**. ambigel; **c**. xerogel.

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**Ex-situ FTIR spectroscopy.** We performed ex-situ FTIR spectroscopy to assess the presence of residual organics and hydroxyl ions/water in the CeO<sub>x</sub> aerogels subjected to various heat treatments. These samples were analyzed using a spectrometer (Magna-IR, Spectrometer 750, Nicolet) over the wave number range of 4000–400 cm<sup>-1</sup>. These measurements show that residual organics and physisorbed water are eliminated after heating the as-prepared materials in oxygen for 2 h (Figure S2). The C-H bending mode at ~1300 cm<sup>-1</sup> is absent after calcination at 600 °C, however, some carbon (in the form of oxygenated species, probably carbonate) is still present, due to the rapid adsorption of atmospheric contaminants onto the ceria aerogel. In the present work, the calcination temperature is limited to  $\leq 600$  °C.



e S2. FTIR spectra for ceria aerogel: as prepared (bottom), calcined in air at  $300 \,^{\circ}$ C (intermediate) and  $600 \,^{\circ}$ C (top).

Elemental compositions derived by X-ray photoelectron spectroscopy. We performed X-ray photoelectron spectroscopy on samples of the various nanoscopic CeO<sub>x</sub> and CeO<sub>2</sub> (sol–gelderived nanoarchitectures and commercial) to probe their elemental compositions. Although XPS is normally considered a surface analytical technique, in the case of nanoscale materials with domain sizes on the order of 10 nm, such as the materials reported here, XPS provides a reasonable quantification of the elements present. The CeO<sub>x</sub> samples were analyzed on indium foil using a Fisons 220iXL X-ray photoelectron spectrometer (monochromatic Al-K $\alpha$  X-ray, spot size 250 × 1000 µm<sup>2</sup>), and quantification was performed for Ce and Cl. The results are displayed in Table S1.

Ceria architecture	Treatment	Cl:Ce ratio
Aerogel	As-prepared	0.36
600-aerogel	600 °C in air	0.13
Ambigel	As-prepared	0.22
600-ambigel	600 °C in air	0.095
Xerogel	As-prepared	0.54
600-xerogel	600 °C in air	0.16
600-commercial	600 °C in air	0.35

**Table S1.** Relative elemental compositions of nanoscopic  $CeO_x$  and  $CeO_2$  as determined by XPS.<sup>a</sup>

a: Elemental ratios by XPS are accurate to  $\pm 10\%$ .

In these experiments, we can see that the chlorine content in the as-prepared and calcined samples depends on the nature of the architecture. All as-prepared sol–gel-derived nanoarchitectures retain chlorine with binding energies for the  $Cl_{2p_{3/2}}$  peaks indicating both ionic and organic chemical states (the organic form is derived from chlorinated alcohol, which is the

end product of nucleophilic attack on the epoxide). The as-prepared xerogel, which undergoes only one set of rinsing steps (with isopropyl alcohol) retains more chlorine than do the asprepared aerogel (two sets of rinsing steps: isopropyl alcohol and acetone) and the as-prepared ambigel (three sets of rinsing steps: isopropyl alcohol, acetone, and cyclohexane).

Only one chemical state of chlorine remains after calcination in air at 600 °C for all samples, and the binding energy of the Cl2p<sub>3/2</sub> peak is consistent with chloride. Calcination leads to a loss of most of the chloride in the ambigel (Cl:Ce = 0.095), while the aerogel and xerogel samples retain slightly more chloride (Cl:Ce ~ 0.13-0.16). In contrast, even after calcination, the commercial sample retains a large amount of chloride (Cl:Ce = 0.35). The presence of chloride in the commercial sample may affect its resistivity slightly, but should not affect its temporal response when the atmosphere is switched from argon to oxygen (and vice versa).