Supporting Information

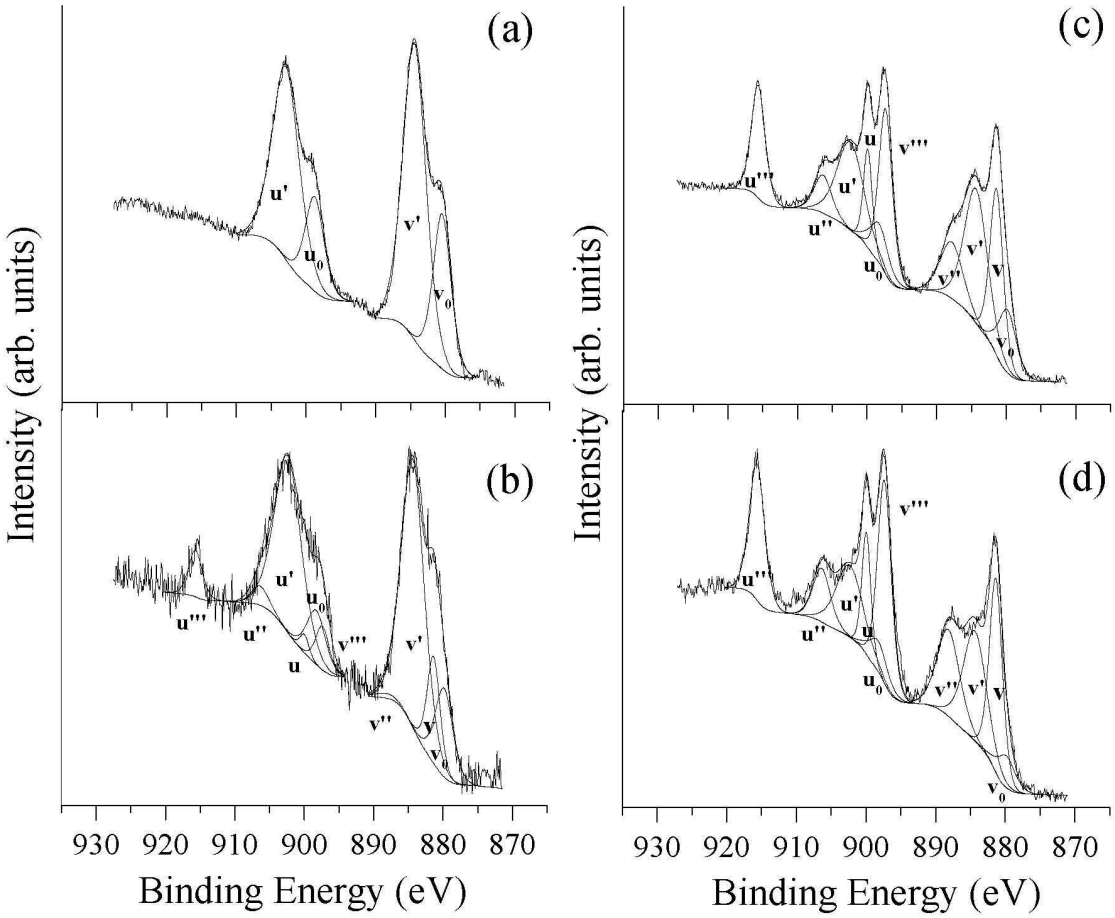

Figure S1: Ce 3d x-ray photoelectron spectra for the as prepared material after more than 5 hours x-radiation, (b) and after ~15 minutes x-radiation. Calcined sample after more than 5 hours x-radiation, (c) and after ~15 minutes x-radiation, (d).

Calculation of the oxidation state of cerium.

The cerium 3d photoelectric spectra are complex comprising a rich satellite structure. The labeling of the spectra in figure S1 follow the notation of Burroughs *et al* [1] with *u* and *v* corresponding to the Ce $3d_{5/2}$ and Ce $3d_{7/2}$ spin-orbit split components respectively. Cerium (III) spectra are known to contain two spin orbit split components labeled in figure S1 as v_0, u_0 and v',u', While cerium (IV) compounds are known to contain three

spin-orbit split pairs and are labeled as *v*, *u*, *v''*, *u''* and *v'''*, *u'''*, detailed descriptions regarding initial and final state peak assignments can be found elsewhere[2]. A complication regarding the assignments of cerium oxidation states due to photoreduction during the XPS experiment has been noted elsewhere [3,4] and was also observed in the present study. Figure S1 shows spectra that were collected after a significant amount of time under x-rays more than 5 hours, as compared to spectra collected after only 15 minutes exposure to x-rays for the as prepared sample (a) and (b) and after calcination (c) and (d).

Table S1 contains the details of the peak fitting shown in figure S1. All spectra were calibrated to the v^1 component at 884.5 eV and fit to peaks with a 50% Gaussian, 50% Lorentzian line shape after application of a Shirley background. Spectra a and c in figure S1 show data collected from the as prepared material after more than 5 hours exposure to x-radiation, these spectra have good signal to noise statistics and the fits obtained from these spectra are used as the basis for the fits to the data collected under minimal exposure to x-radiation where the signal to noise is not as good. The spectrum in figure S1a can be fit to 4 peaks and is consistent with cerium(III) , the absence of a peak at ~916 eV shows no cerium (IV) is present. The peak separation and FWHM values obtained from the fitting of spectrum 3a were used in the fitting of the spectrum in 3 (c),, this spectrum containing a total of 10 peaks corresponding to a mixture of Ce(III) and Ce(IV) oxidation states. The binding energy positions and FWHM values obtained from the fitting of spectrum 3(c) are given in table S1, these values were then used to fit the remaining two spectra. Both binding energy positions and FWHM values are consistent with those reported previously for Ce (III) and (IV) compounds.[1-4]

Ce $3d_{7/2}$	v_0 Ce^{3+}	v Ce^{4+}	v' Ce^{3+}	v'' Ce^{4+}	v''' Ce^{4+}
Binding Energy (eV)	880.3	881.9	884.8	888.3	897.8
FWHM (eV)	3.0	2.2	3.9	3.8	2.3
Ce $3d_{5/2}$	u_0 Ce^{3+}	u Ce^{4+}	u' Ce^{3+}	u'' Ce^{4+}	u''' Ce^{4+}
Binding Energy (eV)	898.8	900.4	902.9	906.8	916.1
FWHM (eV)	3.2	1.5	4.5	2.9	2.3

***Table S1*:** The binding energy positions and FWHM values obtained from the fitting of spectrum 3(c)

The ratio of oxidation states can be calculated by adding together the contribution from the peaks due to the different oxidation states as follows

Ce(III) = $Iv_0 + Iu_0 + Iv + Iu'$ and Ce (IV)= $Iv + Iu + Iv'' + Iu'$ '$+ Iv''' + Iu'''$

Where I is the area under the peak

$$\%\,Ce(III) = \frac{Ce(III)}{Ce(III) + Ce(IV)} \times 100$$

The % compositions as calculated from the spectra collected under x-radiation for ~15 minutes for the as prepared sample is 81% Ce(III) and 19% Ce(IV) and for the sample after calcination 33% Ce(III) and 67% Ce(IV). After exposure to x-radiation for more than 5 hours the as prepared sample was found to have undergone photoreduction to an extent that there was no evidence of Ce(IV) in the spectrum, while the sample after calcinations showed an increased in the percentage of Ce(III) to ~ 45%.

References

1. Burroughs, P.; Hammett, A.; Orchard, A. F.; Thornton, G., *J. Chem. Soc.*, *Dalton Trans.* **1976**, *17*, 1686.
2. Mullins, D. R.; Overbury, S. H.; Huntley, D. R., *Surf. Sci.* **1998**, *409*, 307.
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4. Suchorski, Y.; Gottfriedsen, J.; Wrobel, R.; B. Strzelczyk, Weiss, H., *Solid Stae Phenomena* **2007**, *128,* 1794.