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Supporting Information

The Role of Surface Lattice Defects of $CeO_{2-\delta}$ Nanoparticles as Scavenging Redox Catalyst in Polymer Electrolyte Membrane Fuel Cells

Aniket Kumar[†a], Jae-Woon Hong[†a], Yejin Yun[a], Aman Bhardwaj[a] and Sun-Ju Song[a]*

[†]These authors contributed equally.

[a]Ionics Lab, School of Materials Science and Engineering, Chonnam National University, Buk-gu, Gwang-Ju 500-757, Korea.

Figure Summary

Figure S1. (a) XRD pattern of $CeO_{2-\delta}$ nanoparticle at different time i)24h, ii) 48 h and iii) 72 h and (b) Error bars represent standard deviations of the mean particle sizes determined by XRD peak broadening.

Figure S2. (a) XRD pattern of $CeO_{2-\delta}$ nanoparticle at different calcination temperature 100-750 °C

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Figure S8. Raman spectra for $CeO_{2-\delta}$ nanoparticle calcined for 24 hours at a) 100 °C under O_2, b) 100 °C under H_2, c) 350 °C under H_2 and d) 750 °C under H_2 atmosphere.

Table S1 Calculated values of lattice strain and mean crystallite size (D)

Table S2. Calculated value of Ce^{3+} and Ce^{4+} concentration from deconvoluted peaks area

Literature Cited (page S17-S18)

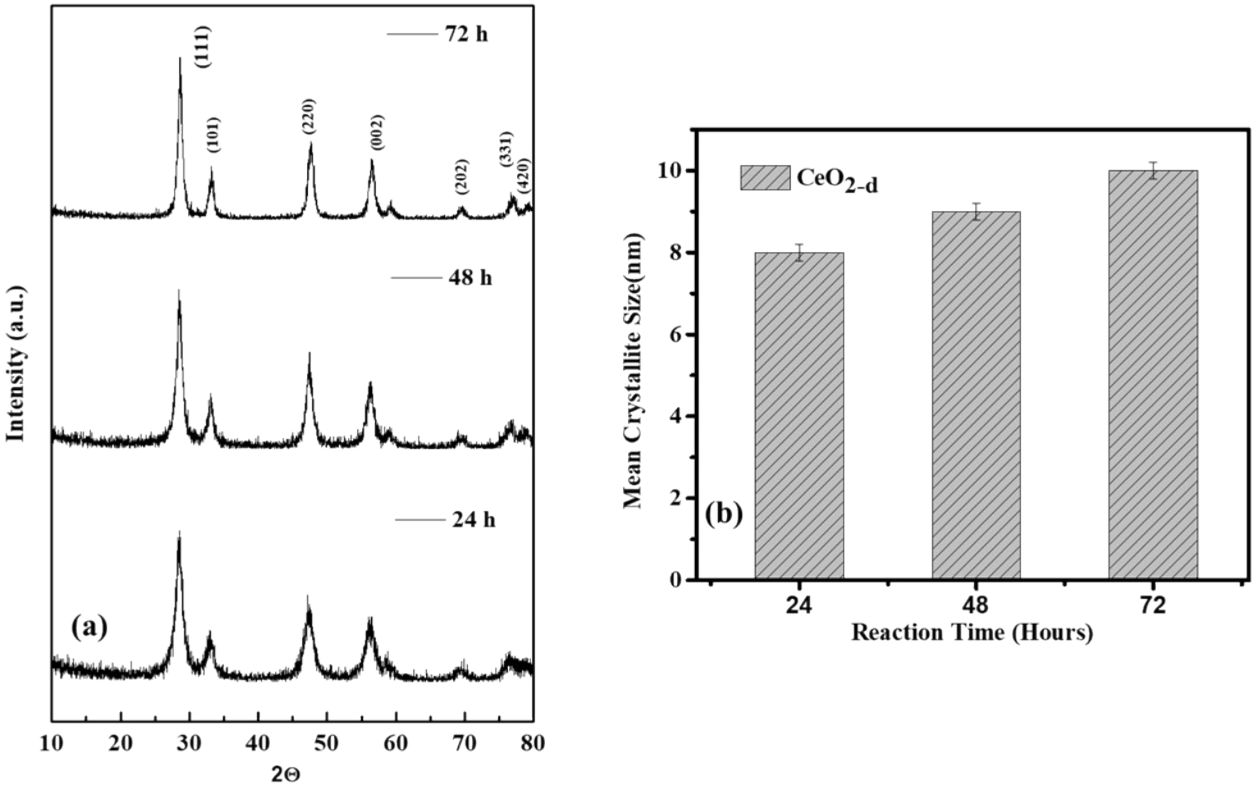

Figure S1. (a) XRD pattern of $CeO_{2-\delta}$ nanoparticle at different time i)24h, ii) 48 h and iii) 72 h and

(b) Error bars represent standard deviations of the mean particle sizes determined by XRD peak broadening.

The scherrer's equations was employed to calculate the crystallite size of each ceria samples synthesized at different reaction time. The scherrer's equation is represented as:

$$d = \frac{0.9\lambda}{\beta cos\theta}$$

Where d is represent crystallite size, λ represent the wavelength of light source used, θ is the angle of diffraction, and β is full width at half maximum (FWHM). The overall broadening of diffraction peak in XRD is mainly contributed from structural and instrumental broadening. The broadening of XRD peaks of CeO_2 nanoparticles suggest about amorphous grain boundary.

Further on going insight to find other reason responsible for broadening of XRD peaks with varying reaction time, Williamson-Hall equation was utilized. From this equation lattice strain is calculated which is induced due to change in crystallite size leading to line broadening. Presuming that the particle size and strain involvement to the line broadening are independent to each other, then the observed line broadening is represented by

$$\beta_{hkl} cos\theta = \frac{K\lambda}{D} + 4\epsilon\ sin\theta$$

Where ε is the micro strain and D is the size of crystallite. For the calculation of strain, $\beta_{hkl} cos\theta$ is contrived against $4\epsilon\ sin\theta$ and the attained points are linearly fitted. The slope of this linear decent gives the standards for effective strain and intercept gives the effective crystallite size.[1]

Table S1 Calculated values of lattice strain and mean crystallite size (D)

λ(nm)	θ(degree)	β(radian)	cosθ	K λ	βCosθ	Mean Crystallite Size(D)	Lattice Strain (%)
0.154	0.975	0.0170	0.969	0.1386	0.0165	8 nm (24 h)	0.70
0.154	0.865	0.0151	0.969	0.1386	0.0146	9 nm (48 h)	0.60
0.154	0.78	0.0136	0.969	0.1386	0.0132	10 nm (72 h)	0.42

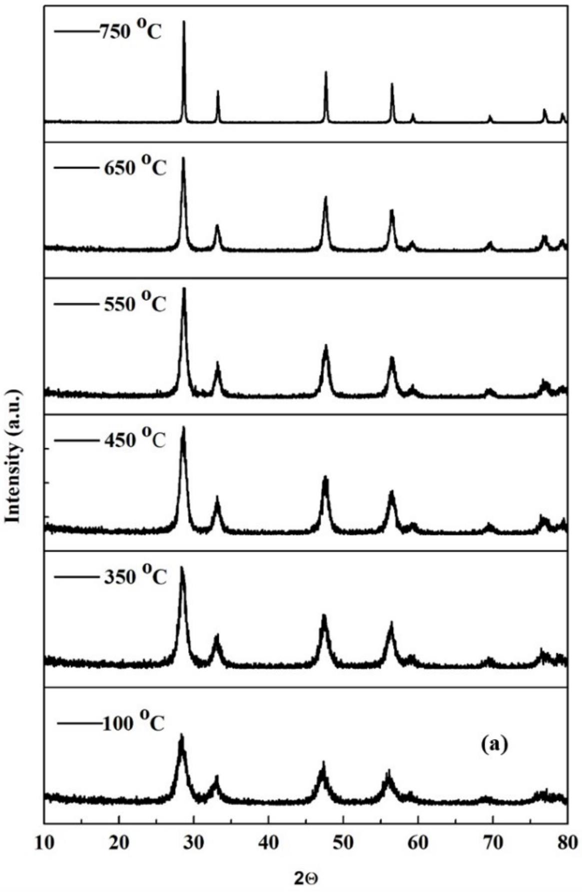

Figure S2. (a) XRD pattern of $CeO_{2-\delta}$ nanoparticle at different calcination temperature 100-750 °C

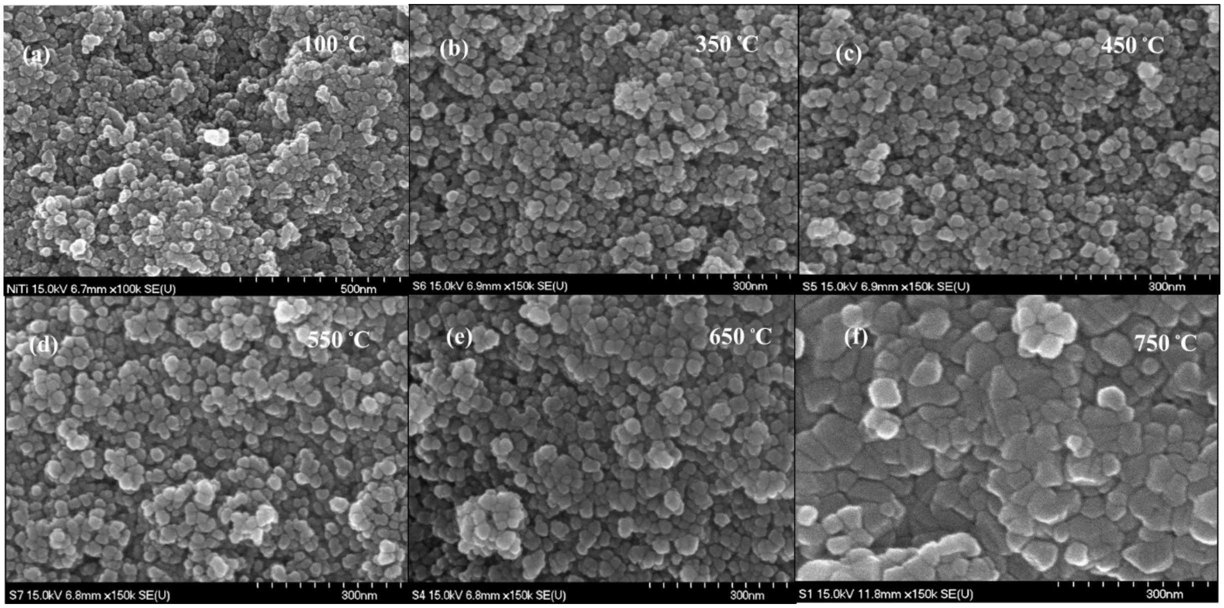

Figure S3. FE-SEM analysis of $CeO_{2-\delta}$ nanoparticles at different calcination temperatures (100-750 °C).

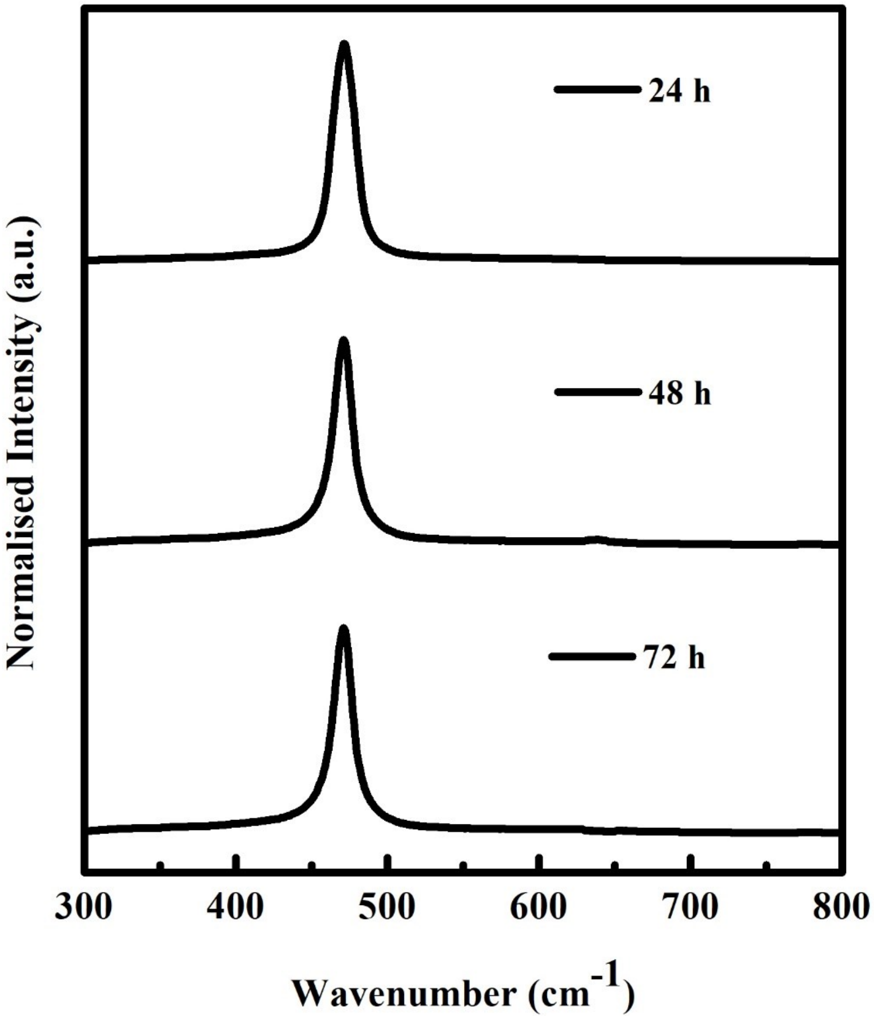

Figure S4. Raman spectrum of nano $CeO_{2-\delta}$ obtained by changing reaction time from 24h to 72 h.

The figure S4 present the Raman spectra of $CeO_{2-\delta}$ nanoparticle showing as intense peak at 467cm^{-1}. This peak featured is assigned for symmetrical stretching mode for Ce-O_8 vibrational mode.[2] Therefore it is well assumed that this manner of peak is very sensitive for monitoring any kind of disorderness in oxygen sub lattice consequential from thermal and/or grain size induced non-stoichiometry. The minute change in microstructure of $CeO_{2-\delta}$ nanoparticle by changing different parameter such as reaction time and temperature affect the shape of Raman spectra significantly. The microstructure change result in broadening in Raman peaks suggesting reduction of the phonon lifetime in the nanocystalline regime.[3–5] The Raman line (467 cm^{-1}) broadening can be described by correlating half width at half-maximum (HWHM) on the grain size. This correlation was done by mathematical equation proposed by Weber and co-worker.[3]

$$\Gamma(cm^{-1}) = 5 + \frac{51.8}{d_g(nm)}$$

Where d_g is the grain size and Γ is the HWHM. This equation shows the dependence of the half-width of Raman line as a function of the inverse of grain size. Further the grain size was correlated with correlation length (L). Correlation length gives us information about the average distance between two lattice defects. Finally the concentration of oxygen vacancies was estimated by applying spatial correlation model.[4,6]

$$\mathrm{L\ (nm)} = \sqrt[3]{(\frac{a}{2d_g})^2[(d_g-2\alpha)^3+4d_g^2\alpha]}$$

Where L is the correlation length and α the radius of $CeO_{2-\delta}$ units (0.34nm) calculated from applying universal constants.[2] The defect concentration (N) was lastly correlated with correlation length mathematically using equation.[2,3]

$$\mathrm{N\ (cm^{-3})} = \frac{3}{4\pi L^3}$$

Figure S5. (a) Raman spectra of $CeO_{2-\delta}$ nanoparticle with different calcination temperature.

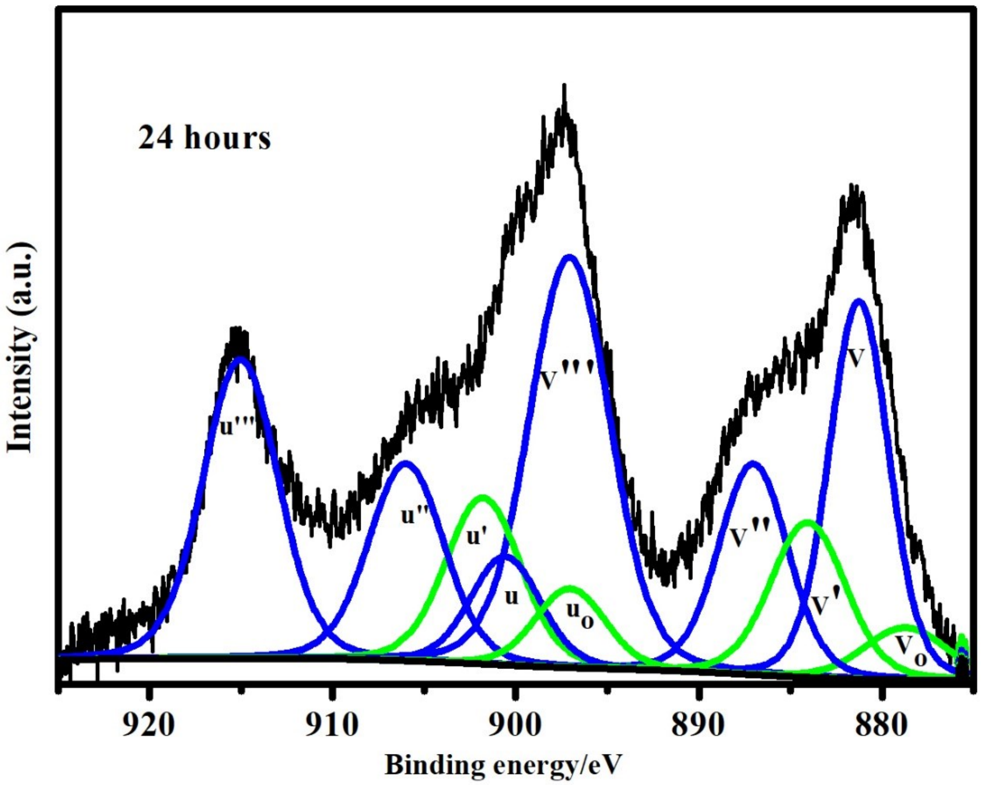

Figure S6. Deconvoluted XPS elemental scan for Ce3d of $CeO_{2-\delta}$ nanoparticle after 24 hours.

X-ray photoelectron technique (XPS) is a vital technique from which we can quantitatively measure the different electronic state of cerium (Ce^{3+} and Ce^{4+}) in $CeO_{2-\delta}$ nanoparticle. The XPS spectra is mainly obtained by bombarding the particles with X rays and simultaneously measuring the kinetic energy of electron irradiated from it. Most of the electrons are ejected inside from few atomic layers of the surface. It is well assumed that as the particles are in nanometric range, the ejection of electrons are from surface and bulk have no significant impact. Because the bulk and surface concentration tend to be same in nanometric range for particles.

To correlate the impact of reaction time and calcination temperature over oxidation state of cerium, XPS analysis was carried on using X-ray photoelectron spectrometer((Multi Lab 2000, Thermo VG Scientific, United Kingdom). XPS spectra were recorded in the interval 875-925 eV. Firstly the spectra were corrected by baseline subtraction. The position of the well resolved peak u’” (at around 915 eV) in the spectra was deconvulated first and then other peaks were separated out and fixed. The relative deconvulated peak position are shown in table S6. The casa XPS software for raw data fitting. The results obtained were similar to reported literature.[6, 7]

The total concentration of Ce^{3+} and Ce^{4+} in the samples has been considered using the following formula.[9]

$$\% \, [Ce_{Ce}^{'}] = \left[\frac{A_{Ce_{Ce}^{'}}}{A_{Ce_{Ce}^{'}}} + \frac{A_{Ce_{Ce}^{'}}}{A_{Ce_{Ce}^{x}}} \right] x100\%$$

$$\%[Ce_{Ce}^{x}] = \left[\frac{A_{Ce_{Ce}^{x}}}{A_{Ce_{Ce}^{'}}} + \frac{A_{Ce_{Ce}^{x}}}{A_{Ce_{Ce}^{x}}} \right] x100\%$$

Here $A_{Ce^{3+}} = V_o + V^{'} + u_o + u^{'}$ and $A_{Ce^{4+}} = V + V^{''} + V^{'''} + u + u^{''} + u^{'''}$ are the summation of combined area of all feature peaks of Ce^{3+} and Ce^{4+}, respectively. These sequences of peaks are considered as "*u*" and "*v,*" which arising due to $3d_{3/2}$ and $3d_{5/2}$ spin–orbit states, respectively. Herein the symbols $V_o, V^{'}, u_o and\ u^{'}$ refer to the XPS peaks associated with binding energies of 3d electrons in Ce^{3+} and $V, V^{''}, V^{'''}, u, u^{''} and\ u^{'''}$ are the peaks related to 3d electrons in Ce^{4+}.[10]

Table S2. Calculated value of Ce^{3+} and Ce^{4+} concentration from deconvoluted peaks area.

Sample	$Ce3d_{5/2}$					$Ce3d_{3/2}$					$\% \, [Ce_{Ce}^{'}]$	$\%[Ce_{Ce}^{x}]$	$[Ce_{Ce}^{'}]/[Ce_{Ce}^{x}$
	V_o	V	$V^{'}$	$V^{''}$	$V^{'''}$	u_o	u	$u^{'}$	$u^{''}$	$u^{'''}$			
$CeO_{2-\delta}$ (24h)	878.6	881.2	884	887.1	897.1	896.8	901.1	902.2	905.9	914.9	12.72	87.28	0.145
$CeO_{2-\delta}$ (48h)	878.8	881.7	884.1	887.3	897.8	897.1	901.4	902.2	906	914.9	12.16	87.84	0.138

$CeO_{2-\delta}$ (72h)	878.2	881.5	883.9	887.5	897.6	896.7	901.7	902.5	905.8	915.4	11.23	88.77	0.126

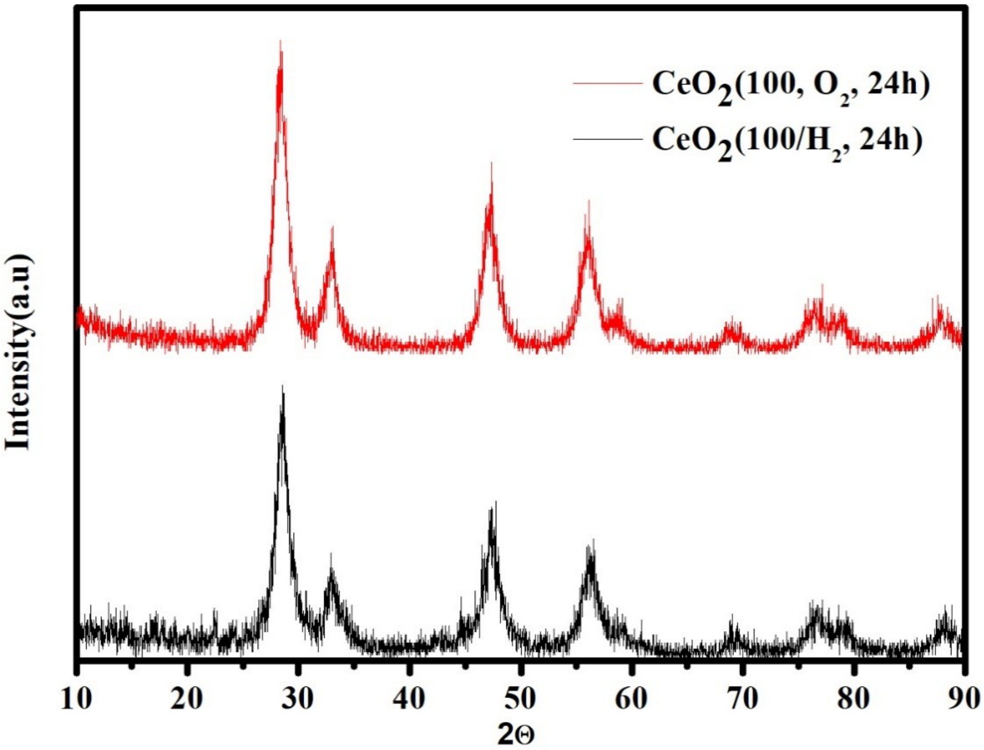

Figure S7. XRD foe $CeO_{2-\delta}$ nanoparticle calcined for 24 hours at 100 °C under O_2 and H_2 atmosphere.

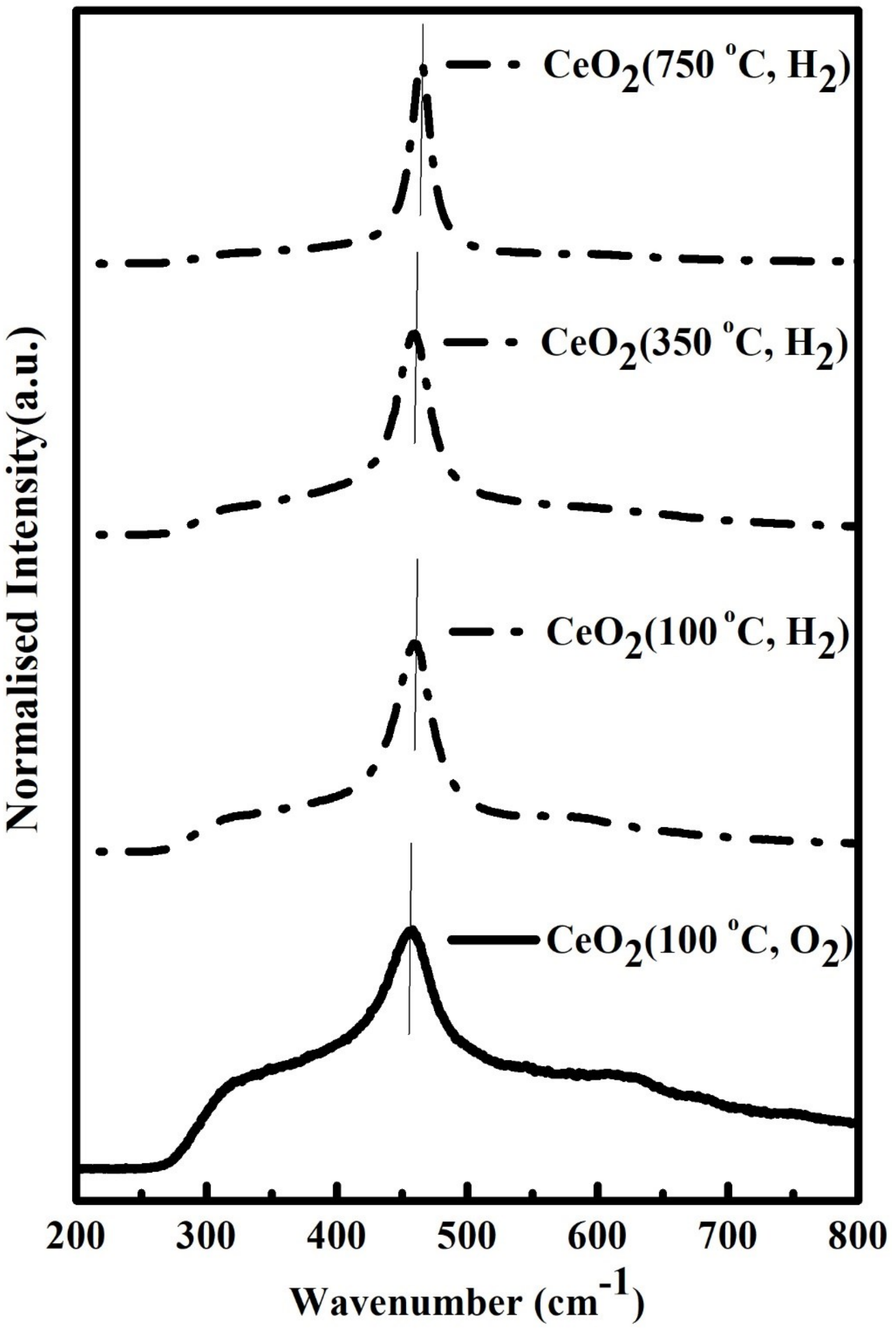

Figure S8. Raman spectra for $CeO_{2-\delta}$ nanoparticle calcined for 24 hours at a) 100 °C under O_2, b) 100 °C under H_2, c) 350 °C under H_2 and d) 750 °C under H_2 atmosphere.

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