

Supporting Information

Autonomous self optimizing defects by refining energy levels through hydrogenation in CeO_{2-x} polymorphism: A walking mobility of oxygen vacancy with enhanced adsorption capabilities and photocatalytic stability

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Fig. S1 Comparison between successive Ce 3d XPS spectra of CeO_{2-x} and H- CeO_{2-x} catalyst

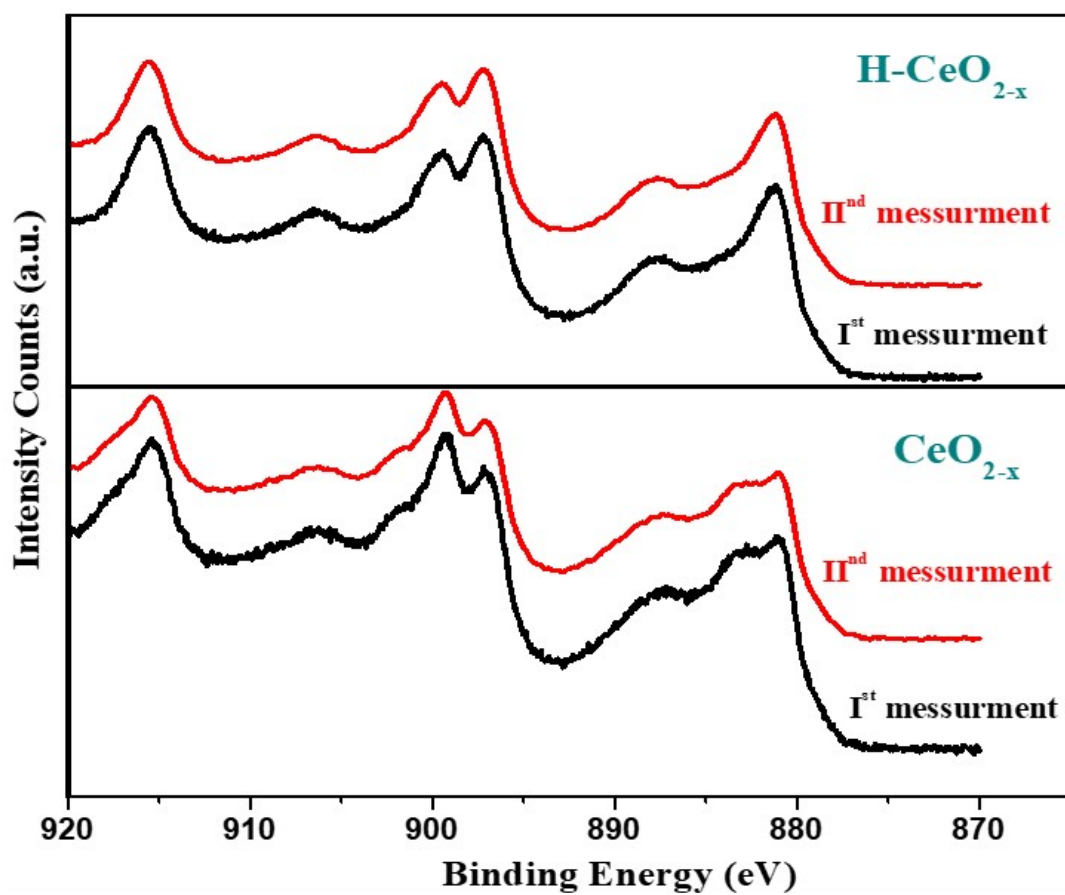


Fig. S2. The quantitative concentration as well as ratio of the $[\text{Ce}^{4+}]/[\text{Ce}^{3+}]$ in CeO_{2-x} and H- CeO_{2-x} catalyst were calculated using Eq. 1. The concentration of Ce^{3+} was calculated by taking the ratio of the integrated peak areas corresponding to the Ce^{3+} peaks to the total area under the whole $\text{Ce}3d$, i.e. $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ spectrum. The Ce^{3+} concentration in CeO_{2-x} and H- CeO_{2-x} samples is calculated using equation Eq. 1.

$$\text{Ce}^{3+} = \frac{A_{vo} + A_{v'} + A_{uo} + A_{u'}}{A_{vo} + A_{v'} + A_{uo} + A_{u'} + A_v + A_{v''} + A_{v'''} + A_u + A_{u''} + A_{v'''}} \quad (1)$$

where A denotes the area of the corresponding peaks marked as the subscript in the spectrum (Fig 4 (c)). The calculated concentration of Ce^{3+} in CeO_{2-x} and H- CeO_{2-x} is $\sim 44.6\%$ and $\sim 36.3\%$. Thus, after hydrogenation, the concentration of Ce^{3+} decreases suggesting the conversion of some Ce^{3+} to Ce^{4+} by converting the highly disordered CeO_{2-x} close to more perfect optimized CeO_2 catalyst. It corroborates the XRD results as well. The Ce^{3+} may either be distributed in regions of Ce_2O_3 or around O vacancies in CeO_2 . The $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio in the CeO_{2-x} and H- CeO_{2-x} samples was calculated from the deconvoluted peak area [Fig. (d)]. The decrease in Ce^{3+} concentration caused by hydrogenation may be either due to the reduction of defects, oxygen vacancy or may be Ce_2O_3 phase convert to more stable CeO_2 phase. To further support our results, the total oxygen content in CeO_{2-x} and H- CeO_{2-x} sample is calculated to examine whether the Ce^{3+} has the form Ce_2O_3 or is due to O vacancies. The total oxygen content is the sum of the O required to fully oxidize into Ce^{4+} or to Ce^{3+} and to form CeO_2 and Ce_2O_3 , respectively.

The stoichiometry $X = [\text{O}]/[\text{Ce}]$ is equal to 2 for perfect CeO_2 lattice structure and 1.5 for Ce_2O_3 , the ratio of the required oxygen to fully oxidize Ce^{4+} and Ce^{3+} to the sum $[\text{Ce}^{4+}] + [\text{Ce}^{3+}]$ is determined from the concentrations Ce^{4+} and Ce^{3+} using Eq 2 and are summarized in Table 1

$$X = \frac{[\text{O}]}{[\text{Ce}]} = 3/2 \times [\text{Ce}^{3+}] + 2 \times [\text{Ce}^{4+}].$$

The actual stoichiometry $X' = [O]/[Ce]$ can be calculated directly from the integrated areas of XPS peaks for the $O1s$ and $Ce3d$ according to the equation (3)

$$X' = \frac{O1s}{Ce3d} = \frac{A_O}{A_{Ce}} \cdot \frac{S_O}{S_{Ce}} \quad \text{----- (Eq. 3)} \quad (3)$$

where A_O and A_{Ce} are the integrated areas of the $O1s$ and $Ce3d$ XPS peaks, and S_{Ce} (=7.393) and S_O (=0.711) are sensitivity factors of Ce and O atoms respectively. [15, 29].

Table S1: Concentrations of Ce^{4+} and Ce^{3+} ions, stoichiometry $x = [O]/[Ce]$ and $x' = [O1s]/[Ce3d]$ of the CeO_{2-x} and H- CeO_{2-x} catalyst

Sample	Ce^{4+}	Ce^{3+}	$[Ce^{4+}]/[Ce^{3+}]$	X=	X'=
				$[O]/[Ce]^a$	$[O1s]/[Ce3d]^b$
CeO_{2-x}	0.6373	0.2901	2.196	1.927	2.215
H- CeO_{2-x}	0.7170	0.2421	2.961	1.812	1.982

(where “a” means using the intensities of the $O1s$ and $Ce3d$ XPS peaks and “b” means using the deconvolution of the $Ce3d$ XPS peak).

XPS study confirmed the coexistence of both Ce^{4+} and Ce^{3+} in the samples. This result indicates that H- CeO_{2-x} samples having less concentration of Ce^{3+} caused by oxidation by converting Ce^{3+} to Ce^{4+} in which the most prominent Ce^{4+} content is forming CeO_2 . On the other hand, It is further seen that there is oxygen deficiency w.r.t the required O needed to fully oxidize Ce in CeO_{2-x} with high Ce^{3+} content, suggesting that Ce_2O_3 and O vacancies coexist. However, the maximum oxygen deficiency is ~11% (CeO_{2-x}) and ~4% (H- CeO_{2-x}) thus the majority ~89% of Ce^{3+} is consumed in Ce_2O_3 phase in case of CeO_{2-x} .

Fig. S3). Bar plot showing the remaining concentration of MO solution until the equilibrium of MO over the catalyst under dark

