

## Supporting information

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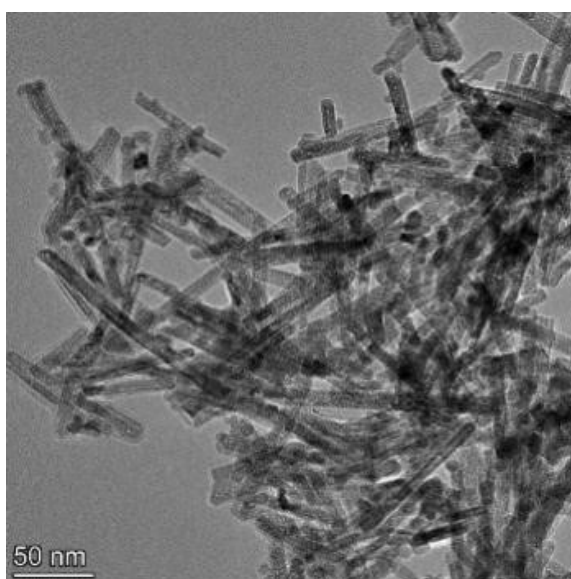


Fig. S1 TEM image of Cu-CeO<sub>2</sub>.

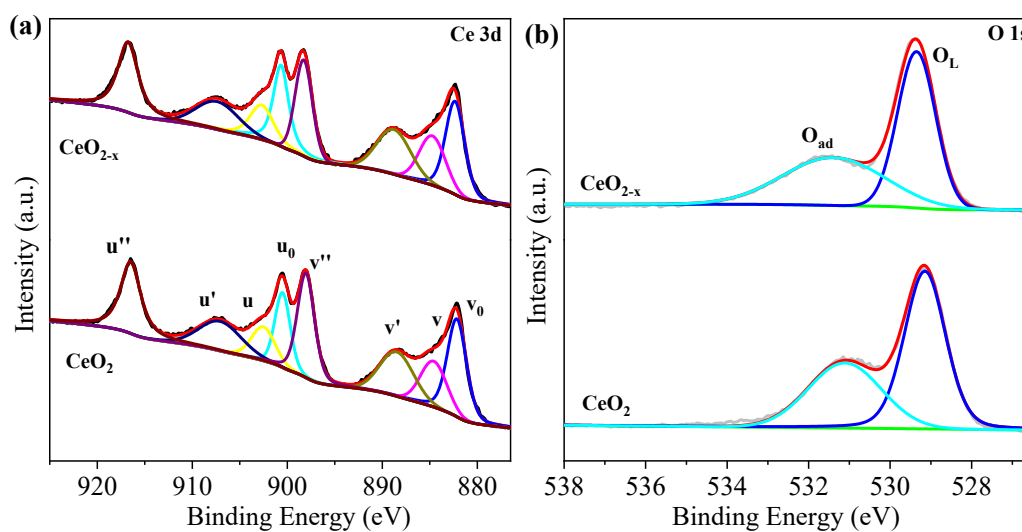
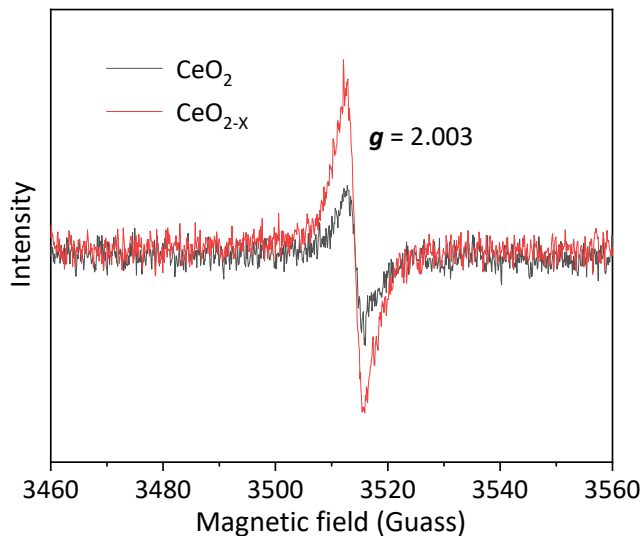


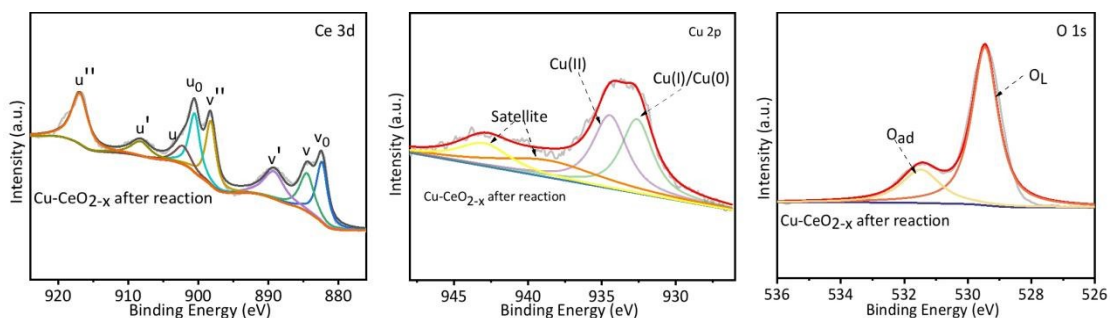
Fig. S2 (a) Ce3d spectra of CeO<sub>2</sub> and CeO<sub>2-x</sub>. (b) O1s spectra of CeO<sub>2</sub> and CeO<sub>2-x</sub>.



**Fig. S3** EPR spectra of  $\text{CeO}_2$  and  $\text{CeO}_{2-x}$

**Table. S1** XPS analysis of  $\text{CeO}_2$  and  $\text{CeO}_{2-x}$

Sample	$\text{CeO}_2$	$\text{CeO}_{2-x}$
$\text{Ce}^{3+}/\text{Ce}^{4+}$	0.80	0.93
$\text{O}_{\text{ad}}/(\text{O}_{\text{ad}}+\text{O}_{\text{L}})$	0.40	0.47



**Fig. S4** Ce3d spectra, Cu2p spectra and O1s spectra of  $\text{Cu-CeO}_{2-x}$  after reaction

**Table. S2** XPS analysis of  $\text{Cu-CeO}_{2-x}$  and  $\text{Cu-CeO}_{2-x}$  after reaction

Sample	$\text{Cu-CeO}_{2-x}$	$\text{Cu-CeO}_{2-x}$ after reaction
$\text{Ce}^{3+}/\text{Ce}^{4+}$	0.59	0.58
$\text{O}_{\text{ad}}/(\text{O}_{\text{ad}}+\text{O}_{\text{L}})$	0.41	0.40
$(\text{Cu}^0+\text{Cu}^+)/\text{Cu}$	0.84	0.87

**Table S3** The performance of various Cu-MO<sub>x</sub> catalysts for CO<sub>2</sub> electrochemical reduction

Catalyst	Production	Faradic efficiency	Potential	Current density	Electrolyte	Reference
Cu-CeO <sub>2-x</sub>	CH <sub>4</sub>	52.7%	-1.8 V vs. RHE	24.2 mA cm <sup>-2</sup>	0.1 M KHCO <sub>3</sub>	This work
Cu-CeO <sub>2</sub> -4%	CH <sub>4</sub>	58%	-1.8 V vs. RHE	28 mA cm <sup>-2</sup>	0.1 M KHCO <sub>3</sub>	1
Cu/CeO <sub>2</sub> -R	CH <sub>4</sub>	49.3%	-1.6 V vs. RHE	16.8 mA cm <sup>-2</sup>	0.1 M KHCO <sub>3</sub>	2
5-CuO/CeO <sub>2</sub>	CH <sub>4</sub>	37.8%	-1.27 V vs. RHE	22 mA cm <sup>-2</sup>	0.1 M KHCO <sub>3</sub>	3
Cu/CeO <sub>2</sub>	CH <sub>4</sub>	42%	-0.89 V vs. RHE	51 mA cm <sup>-2</sup>	1 M KOH	4
Cu <sub>0.04</sub> /CeO <sub>2</sub>	CH <sub>4</sub>	58%	-1.3 V vs. RHE	7 mA cm <sup>-2</sup>	0.1 M KHCO <sub>3</sub>	5
Cu@ZnO	CH <sub>4</sub>	52%	-1.4 V vs. RHE	7 mA cm <sup>-2</sup>	0.1 M KHCO <sub>3</sub>	6

## References

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