**Supporting Information** 

## Cu Oxide Deposited on Shape-Controlled Ceria Nanocrystals for CO Oxidation: Influence of Interface-Driven Oxidation States on Catalytic Activity

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Nano shaped CuO<sub>x</sub>/CeO<sub>2</sub>:



Fig. S1 a) XRD and b) Raman spectra of nano shaped CeO<sub>2</sub> and CuO<sub>x</sub>/CeO<sub>2</sub> catalysts.

CeO2 Morphology	CeO <sub>2</sub>	CuO <sub>x</sub> /CeO <sub>2</sub>
Nano rod (NR)	0.087±0.003	0.233±0.03
Nano cube (NC)	0.020±0.002	0.072±0.001
Nano sphere (NS)	0.025±0.001	0.086±0.003

Table S1 Concentration of defects in the various samples calculated through Raman spectroscopy  $(I(D)/I(F_{2g})$ .



Fig. S2 TGA analysis of nano-shaped a) CeO<sub>2</sub> and b) CuO<sub>x</sub>/CeO<sub>2</sub> catalysts.



Fig. S3 XPS survey spectra of nano-shaped CuO<sub>x</sub>/CeO<sub>2</sub> catalysts.



Fig. S4 X-ray valence band spectra of nano-shaped CuO<sub>x</sub>/CeO<sub>2</sub> catalysts.



Fig. S5 a) Cu LMM and b) O 1s spectra of CuO<sub>x</sub>/CeO<sub>2</sub> catalysts.



Fig. S6 Photographs of the CuO<sub>x</sub>/CeO<sub>2</sub>NR, CuO<sub>x</sub>/CeO<sub>2</sub>NC, CuO<sub>x</sub>/CeO<sub>2</sub>NS catalysts.

Sample name	CuOx/CeO <sub>2</sub> TPR-I	CuOx/CeO2 TPR-	CeO2 TPR-II	Cu dispersion
	(µ.mol/g)	П	(µ.mol/g)	(%)
		(µ.mol/g)		
CuOx/CeO <sub>2</sub> NR	1441	363.7	159.3	31.9
CuOx/CeO2NC	836	256.4	85.5	45.5
CuOx/CeO2NS	1233	532.6	335.8	43.8

Table S2 Sequential H<sub>2</sub>-TPR-I, N<sub>2</sub>O passivation and H<sub>2</sub>-TPR-II of CeO<sub>2</sub> and CuO<sub>x</sub>/CeO<sub>2</sub> catalyst.



Fig. S7 N<sub>2</sub> adsorption-desorption isotherms of nano-shaped CuO<sub>x</sub>/CeO<sub>2</sub> catalysts.



**Fig. S8** In-situ DRIFT analysis of nano-shaped CeO<sub>2</sub> with 20 % O<sub>2</sub>: 80 % He treatment at various temperatures.

Nano-shaped 8 wt. % CuO<sub>x</sub>/CeO<sub>2</sub>:



Fig. S9 XRD spectra of nano-shaped 8 wt. % CuO<sub>x</sub>/CeO<sub>2</sub> catalysts.



Fig. S10 XPS spectra of nano-shaped 8 wt. % CuO<sub>x</sub>/CeO<sub>2</sub> catalysts (a) Ce 3d, (b) Cu 2p.



Fig. S11 CO conversion as a function of temperature of nano-shaped 8 wt. %  $CuO_x/CeO_2$  catalysts. (a)  $8CuO_x/CeO_2NR$  (b)  $8CuO_x/CeO_2NC$  (c)  $8CuO_x/CeO_2NS$ .