

Electronic Supplementary Information

Hematite concave nanocubes and their superior catalytic activity for low temperature CO oxidation

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Experimental section

Preparation

Synthesis of concave α -Fe₂O₃ nanocubes: 2 mmol of Fe(NO₃)₃·9H₂O and 1 mmol of copper acetate (CuOAc₂·H₂O) were dissolved in 10 mL of deionized water to form a homogeneous solution followed by ultrasonic treatment for 10 min. Then 10 mL of NH₃·H₂O (25 wt.%) was added into the solution. After irradiated by ultrasonic waves for another 5 min, the mixture was transferred into a Teflon-lined stainless steel autoclave of 50 mL capacity, sealed and maintained at 140 °C for 16 h. After the mixture was cooled to room temperature naturally, the obtained product was collected and washed several times with deionized water and ethanol, and finally dried at 60 °C for 12 h.

Synthesis of porous α -Fe₂O₃ nanorods: β -FeOOH nanorods precursors were first synthesized by a hydrothermal method.^[1] 1 mmol of FeCl₃·6H₂O and 2 mmol of urea were dissolved in 20 mL of deionized water to form a homogeneous solution followed by ultrasonic treatment for 5 min. The solution was then transferred into a Teflon-lined stainless steel autoclave of 25 mL capacity. The autoclave was sealed and maintained at 120 °C for 10 h. After the mixture was cooled to room temperature naturally, the brown precipitation was collected and washed with deionized water, and finally dried at 60 °C for 12 h to obtain β -FeOOH nanorods. Porous α -Fe₂O₃ nanorods were obtained by calcining the β -FeOOH nanorods at 520 °C in air for 3 h. The SEM and TEM images of β -FeOOH and α -Fe₂O₃ nanorods are shown in Figure S11.

Characterization

The phase and morphology of the products were characterized by X-ray diffraction (XRD, Philips, X'pert PRO) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), scanning electron microscopy (SEM, LEO 1530), and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100). Energy dispersive X-ray (EDX) analyses were obtained using a FEI Tecnai F30 HRTEM. The samples were prepared by dropping ethanol dispersion of samples onto carbon-coated copper TEM grids. High-resolution X-ray photoelectron spectroscopy (XPS) was carried out on a PHI Quantum 2000 ESCA system with monochromatic Al K α radiation. BET-surface area of catalysts was measured by N₂ adsorption using the single point method. [The amount of Cu in \$\alpha\$ -Fe₂O₃ concave nanocubes was measured by inductively coupled plasma spectrometry \(ICP-MS, Agilent 7500ce\).](#)

Catalytic activity measurements

The catalytic activities of different catalysts for CO oxidation were evaluated in a fixed bed quartz tubular reactor. The catalysts (100 mg) were pre-treated at 350 °C for 4 h before placing in the reactor. The reactant gases (1 vol.% CO, 1 vol.% O₂, balanced with nitrogen) went through the reactor at a rate of 60 mL min⁻¹, corresponding to a gas hourly space velocity (GHSV) of 36 000 ml g⁻¹ h⁻¹.

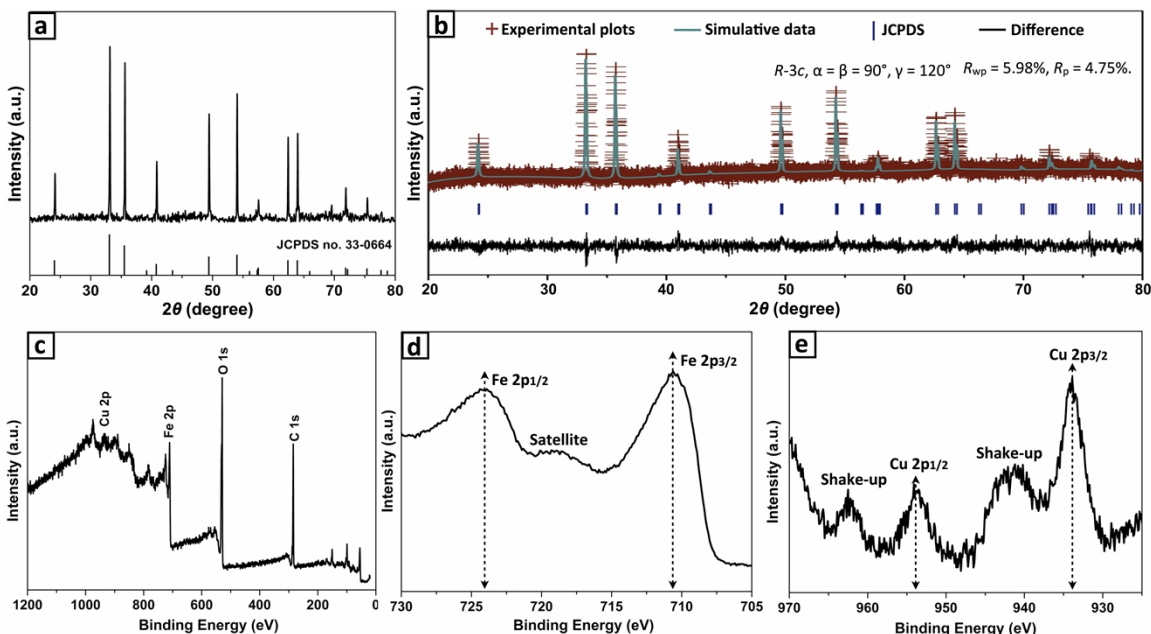


Fig. S1 a) XRD and b) Rietveld XRD patterns of α -Fe₂O₃ concave nanocubes. c) XPS survey spectrum of α -Fe₂O₃ concave nanocubes. d) High resolution XPS spectra of Fe 2p and e) Cu 2p regions for α -Fe₂O₃ concave nanocubes. The XPS analysis shows the evidence of the presence of α -Fe₂O₃ since a satellite peak was observed between Fe 2p_{3/2} and Fe 2p_{1/2} peaks, which is the characteristic of α -Fe₂O₃. The characteristic peaks of Cu 2p at 934.1 eV (Cu 2p_{3/2}) and 953.8 eV (Cu 2p_{1/2}) and their corresponding satellite peaks around 942.4 eV and 962.4 eV clearly indicate the presence of Cu²⁺ ions on the surface of the concave nanocubes.

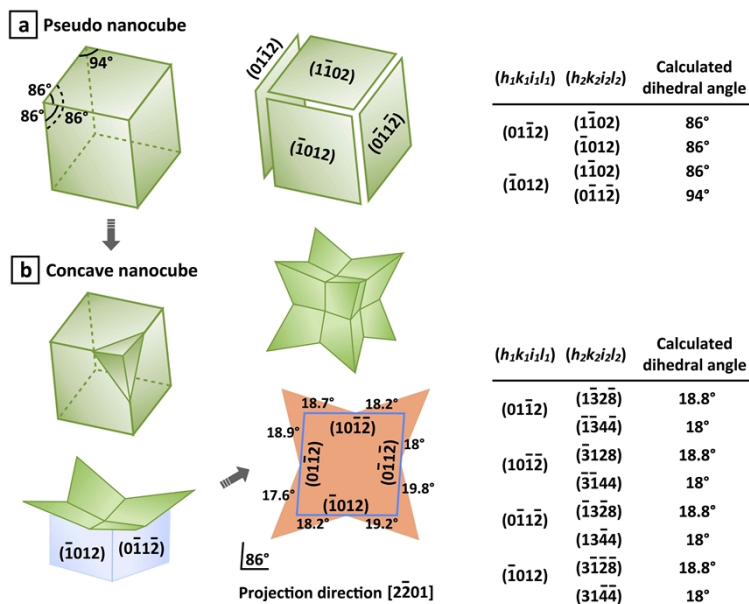


Fig. S2 Geometrical models of α -Fe₂O₃ a) nanocubes and b) concave nanocubes, and their calculated dihedral angles.

The calculation of dihedral angles was based on the experiment results and the theoretical formula as

following:

- the concave nanocubes were evolved from pseudocubic $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals (see the structural evolution presented in Figure 3);
- the nanocubes were bound by six $\{01\text{-}12\}$ facets as shown in Figure S2a and Figure S7;^[2]
- the angles between two crystal facets can be calculated by their Miller indices by the following formula:

$$\cos \phi = \frac{h_1 h_2 + k_1 k_2 + \frac{1}{2}(h_1 k_1 + h_2 k_2) \frac{3a^2}{4c^2} l_1 l_2}{\sqrt{(h_1^2 + k_1^2 + h_1 k_1 + \frac{3a^2}{4c^2} l_1^2)(h_2^2 + k_2^2 + h_2 k_2 + \frac{3a^2}{4c^2} l_2^2)}} \quad (1)$$

According to equation (1), the Miller indices can be determined from the projection angles when the concave nanocubes are viewed along a certain crystallographic direction.

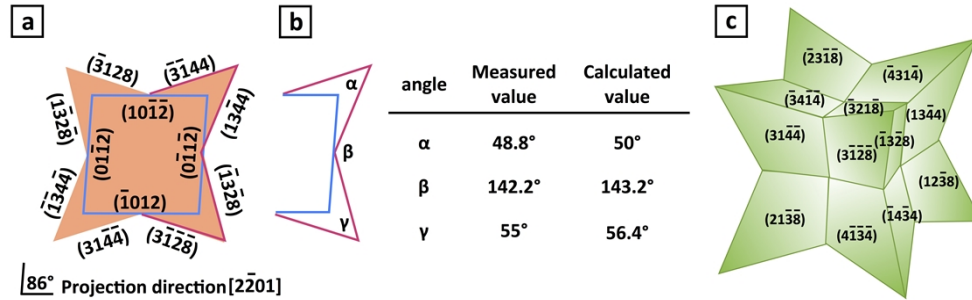


Fig. S3 According to the apex angle of the trigonal pyramidal arms, we can also infer that the exposed facets of the trigonal pyramidal arms are $\{13\text{-}44\}$ and $\{12\text{-}38\}$ facets. The detailed structural models for the as-obtained concave $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals are as follows: a) a 2D model of the concave nanocrystals viewed along the direction $[2\text{-}201]$. The 8 edge-on facets out of 24 facets of a concave nanocube can be indexed as 4 $\{13\text{-}44\}$ and $\{12\text{-}38\}$ facets; b) comparison of the measured values of angles α , β and γ and the calculated values; c) an ideal geometrical model of the concave nanocrystals bounded by 12 $\{13\text{-}44\}$ and 12 $\{12\text{-}38\}$ facets.

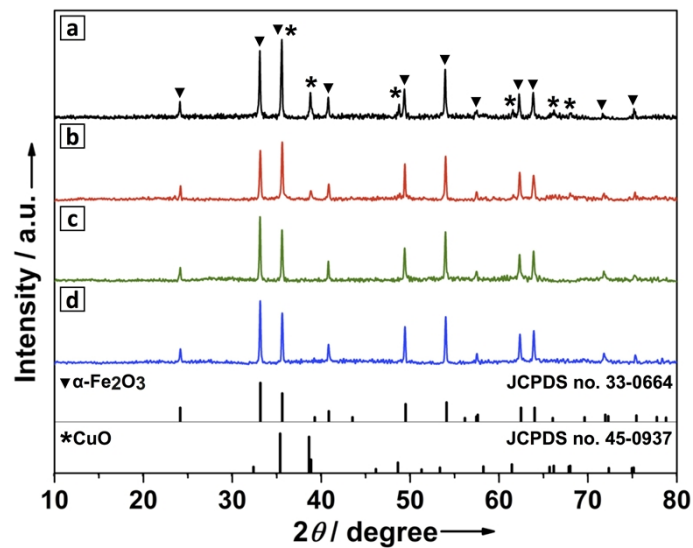


Fig. S4 XRD patterns of the products prepared with different amount of $\text{NH}_3 \cdot \text{H}_2\text{O}$: a) 0.5 mL, b) 1.0 mL, c) 2.0 mL and d) 3.0 mL.

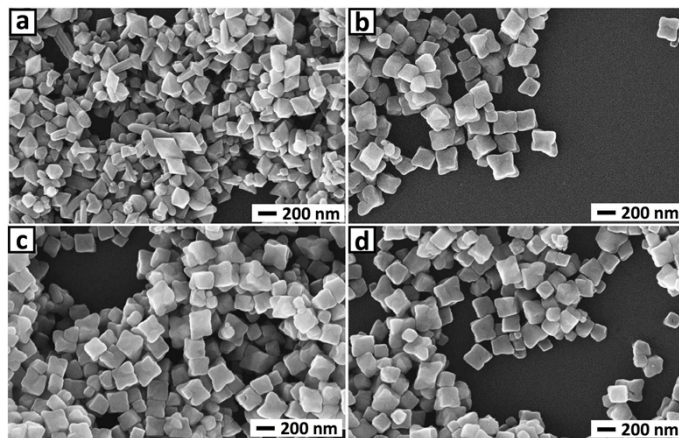


Fig. S5 SEM images of hematite nanocrystals synthesized after hydrothermal treatment with different Cu^{2+} ion sources: a) without the addition of Cu^{2+} , b) CuSO_4 , c) $\text{Cu}(\text{NO}_3)_2$ and d) CuCl_2 .

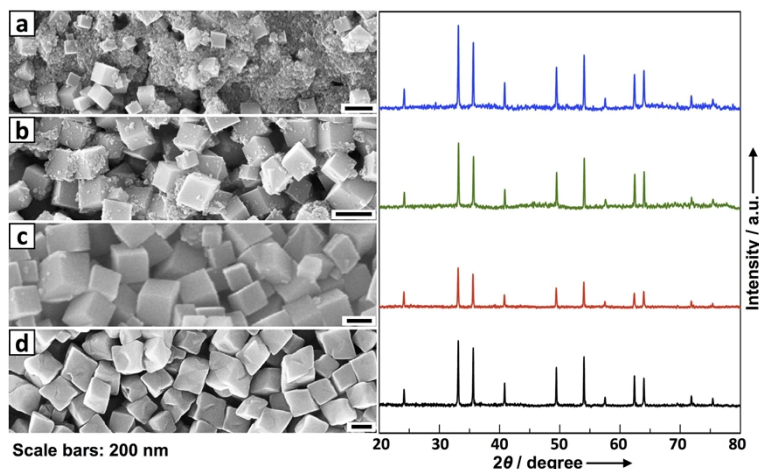


Fig. S6 SEM images and XRD patterns of α -Fe₂O₃ nanocrystals collected after a) 1 h, b) 2 h, c) 6 h, and d) 10 h of hydrothermal treatment. For the SEM and TEM images of the sample collected after 16 h of reaction, please see Figure 1. All the as-obtained samples are pure α -Fe₂O₃ and no other impurities can be detected from their XRD patterns.

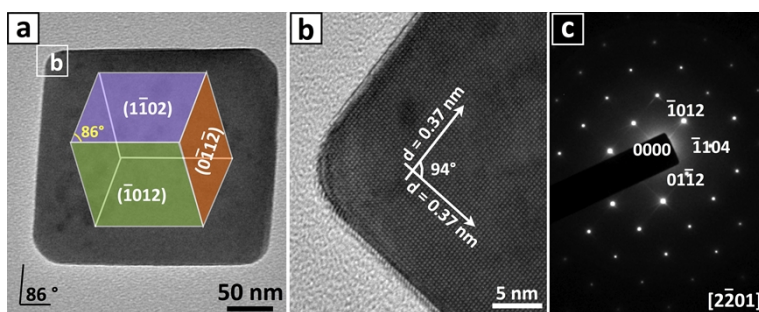


Fig. S7 a) TEM, b) HRTEM images and c) corresponding SAED pattern of a single pseudocubic α -Fe₂O₃ nanocrystal collected after 6 h of hydrothermal treatment. From Figure S7a it can be seen that one of dihedral angles between adjacent facets is 86° . By comparing the measured projected angles with the calculated ones, we can infer that the pseudocubic α -Fe₂O₃ nanocrystals are enclosed by six $\{01\bar{1}2\}$ facets, which is consistent with the results reported by Sugimoto et al. in previous work.^[2]

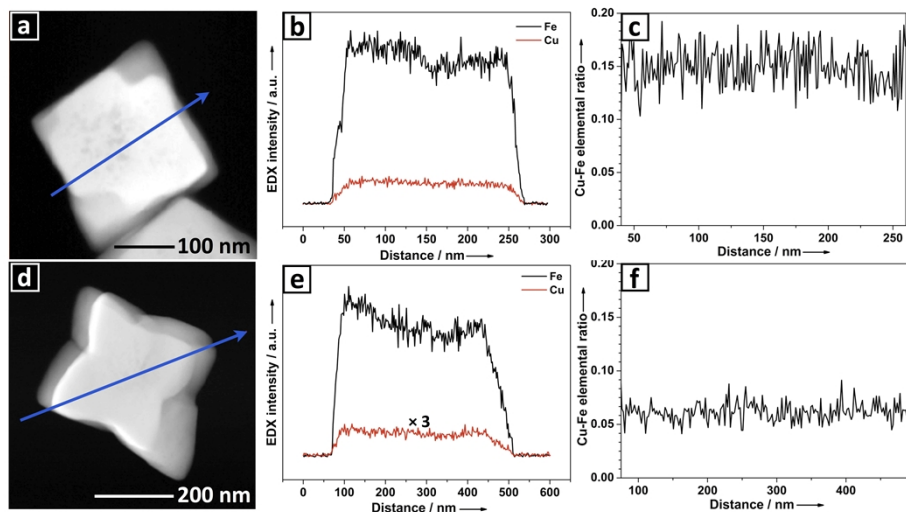


Fig. S8 EDX line profiles of the α -Fe₂O₃ concave nanocubes obtained after different reaction time: a-c) 10 h and d-f) 16 h. The Cu-Fe elemental ratio of the product obtained after 10 h is obviously higher than that of the product obtained after 16 h, suggesting the copper ions dissolve into the bulk solution during the reaction.

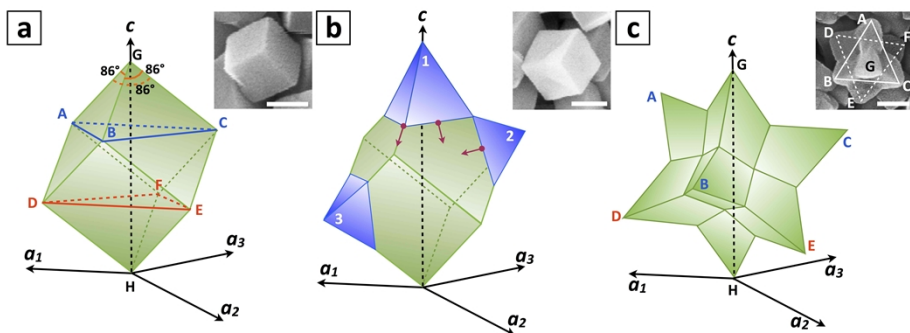


Fig. S9 An overview of a concave hematite nanocube evolved from a pseudocubic nanocrystal set in the hexagonal coordinate. a) 6 h, b) 10 h and c) 16 h. Scale bars: 200 nm. The c -axis of the hexagonal system coincides with the longest diagonal axis (denoted as HG in Figure S9a) of a particle. The growth rate along this direction should be the fastest, and the growth rate along other directions (e.g. directions along six corners marked as A-F) should be theoretically equivalent to each other. The red arrows in Figure S9b show the growth directions of the triangular pyramids.

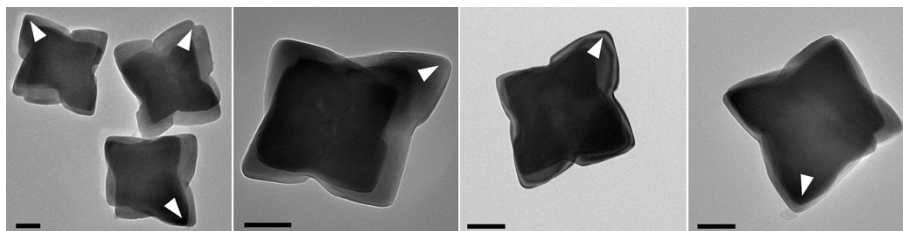


Fig. S10 TEM images of α -Fe₂O₃ concave nanocubes. The white arrows show the direction of *c*-axis of particles, along which the growth rate is obviously much faster than other directions. Scale bars: 100 nm.

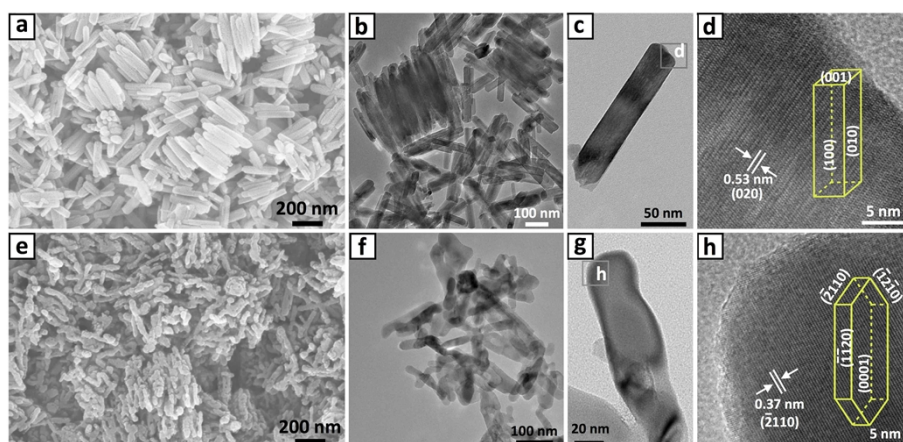


Fig. S11 a) SEM, b, c) TEM, and d) HRTEM images of β -FeOOH nanorods. e) SEM, f, g) TEM, and h) HRTEM images of porous α -Fe₂O₃ nanorods obtained by calcining the β -FeOOH nanorods at 520 °C in air for 3 h. The insets of d) and e) are structural models of β -FeOOH and α -Fe₂O₃ nanorods, respectively.

Table S1. The specific surface areas and pore parameters of α -Fe₂O₃ concave nanocubes and porous nanorods.

α -Fe ₂ O ₃	BET surface area (m ² g ⁻¹)	BJH pore size (nm)	Pore volume (cm ³ g ⁻¹)
Concave nanocubes	13.48	3.86	0.03
Porous nanorods	39.26	6.15	0.15

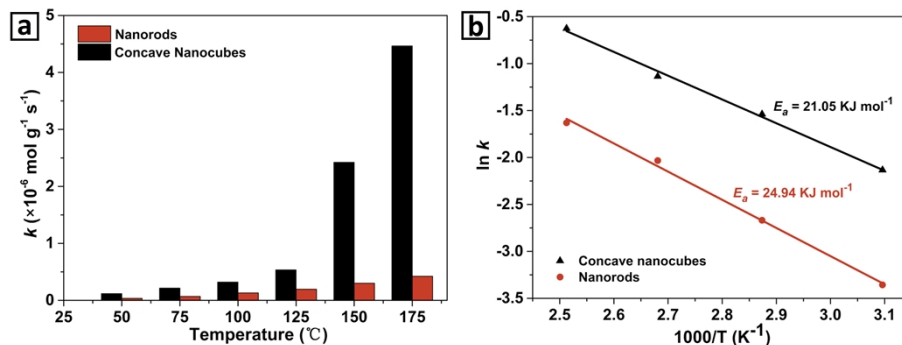


Fig. S12 a)* Specific rates (k) of $\alpha\text{-Fe}_2\text{O}_3$ concave nanocubes and nanorods in CO oxidation. b)** The Arrhenius plots for the reaction activation energy E_a on $\alpha\text{-Fe}_2\text{O}_3$ concave nanocubes and nanorods. Feed gas containing 1 vol.% CO, 1 vol.% O_2 and balance N_2 is at a total flow rate of 60 mL min^{-1} , corresponding to a GHSV of $36\,000 \text{ ml g}^{-1} \text{ h}^{-1}$.

* The values of specific rate of CO oxidation over $\alpha\text{-Fe}_2\text{O}_3$ concave nanocubes and porous nanorods are listed in Table S2.

The specific reaction rate K can be calculated assuming the ideal gas behaviour as follows:

$$K (\text{mol g}^{-1} \text{ s}^{-1}) = \text{GHSV} (\text{mL h}^{-1} \text{ g}^{-1}) \times 1/3600 (\text{h s}^{-1}) \times 1/1000 (\text{L mL}^{-1}) \times \text{CO vol.\%} \times \text{conversion\%} \times 1/22.4 (\text{mol L}^{-1}) \quad (2)$$

**The specific reaction rate could be expressed by the Arrhenius equation:

$$K = A \exp(-E_a/RT) \quad (3)$$

where K is the reaction rate of CO ($\text{mol CO g}^{-1} \text{ s}^{-1}$), A is the pre-exponential factor (s^{-1}), E_a is the apparent activation energy (KJ mol^{-1}), R is the gas constant, and T is the absolute temperature (K). Taking the natural log of both sides of the equation (2), we get:

$$\ln K = -E_a/T + \ln A \quad (4)$$

By plotting $\ln K$ versus $1000/T$, the apparent activation energy E_a can be calculated from the slope as shown in Figure S12b.

Table S2. The values of specific rate of CO oxidation over $\alpha\text{-Fe}_2\text{O}_3$ concave nanocubes and porous nanorods at different reaction temperature.

Temperature ($^{\circ}\text{C}$)	CO conversion (%)		Specific rate ($\times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$)	
	Concave nanocubes	Porous nanorods	Concave nanocubes	Porous nanorods
40	2.65	0.78	0.12	0.03
60	4.81	1.55	0.21	0.07
80	7.19	2.93	0.32	0.13
100	11.98	4.38	0.53	0.20
120	44.24	5.74	1.98	0.26
140	83.26	7.49	3.72	0.33
160	100	10.79	4.46	0.48

Table S3. A comparison of the catalytic performance towards CO oxidation over different catalysts.

Catalyst	GHSV (mL h ⁻¹ g ⁻¹)	Temp. (°C)	CO conversion	Specific rate (× 10 ⁻⁶ mol g ⁻¹ s ⁻¹)	T50% (°C)	T100% (°C)	Ref.
α-Fe ₂ O ₃ concave nanocubes	36 000	120	44.2%	1.98	124	160	This work
α-Fe ₂ O ₃ nanorods	36 000	120	5.74%	0.26	251	340	This work
α-Fe ₂ O ₃ large nanocubes ^[a]	30 000	150	< 3%	< 0.11	470		[3]
α-Fe ₂ O ₃ small nanocubes ^[a]	30 000	150	< 3%	< 0.11	266	350	[3]
Mesoporous CeO ₂ ^[b]	44 400	150	20%	3.33	203	> 300	[4]
CeO ₂ nanorods ^[c]	30 000	150	< 20%		186	275	[5]
CeO ₂ -TiO ₂ ^[d]	39 000	225	10%	0.48	287	> 375	[6]
Ce _{0.5} Fe _{0.5} O ₂ ^[e]	30 000	182	10%	0.37	247	300	[7]
α-Fe ₂ O ₃ /CeO ₂ ^[f]	24 000	250	> 80%	> 1.8	227	400	[8]
Au/CeO ₂ ^[g]	12 000	150	< 40%		175	400	[9]
Pd/α-Fe ₂ O ₃	72 000	150	< 10%		175	200	[10]
Au/α-Fe ₂ O ₃ ^[h]	80 000	150	70%		93	220	[11]

[a] The catalyst was pre-treated at 350 °C for 4 h.

[b] The catalyst was pre-treated at 400 °C for 1 h.

[c] The catalyst was pre-treated at 350 °C for 4 h.

[d] The Ce/Ti mole ratio is 0.40. The catalyst was pre-treated at 500 °C for 2 h.

[e] The catalysts were pre-treated at 600 °C for 4 h in air.

[f] The catalyst was pre-treated at 650 °C for 8 h in air. The Fe molar percentage is 10%.

[g] The support was CeO₂ mesoporous spheres. The catalyst was pre-treated at 350 °C for 1 h.

[h] The support was rhombohedral Fe₂O₃ nanoparticles. The Au loading is 1 wt.%.

For all catalysts, the CO concentration in the fed gas is 1 vol.%.

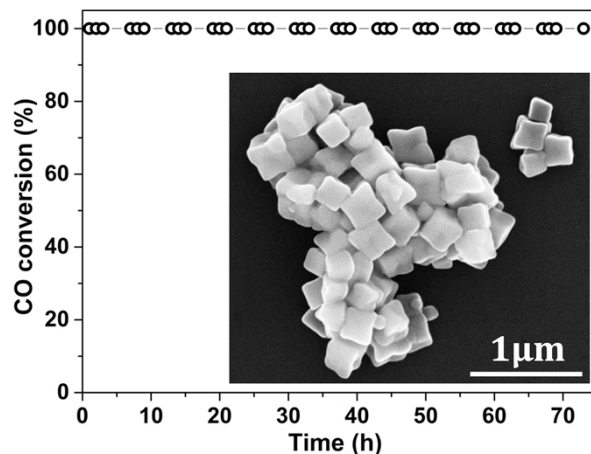


Fig. S13 Stability test of the catalytic CO oxidation over α -Fe₂O₃ concave nanocubes at 160 °C. Feed gas containing 1 vol.% CO, 1 vol.% O₂ and balance N₂ is at a total flow rate of 60 mL min⁻¹, corresponding to a GHSV of 36 000 ml g⁻¹ h⁻¹. The inset shows the SEM image of the α -Fe₂O₃ concave nanocubes after 72 h of reaction.

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