Electronic Supplementary Information (ESI†)

High-efficient Pt catalyst immobilized on hierarchical N-doped carbon nanocages for preferential oxidation of CO in H_2

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Experimental Section

Materials synthesis

The carbon-based nanocages were synthesized at 900 ℃ by the *in situ* MgO template method with respective benzene or pyridine precursor, similar to our previous reports.[1,2] The thickness of carbon layers can be well regulated by changing the dosage of the precursors. After removing the template, the collapsed nitrogen-doped carbon nanocages (cNCNC) were obtained via capillarity compression because of its thin carbon layers. Carbon black (Vulcan XC-72R) was purchased from Acros, denoted as CB.

Supported Pt catalysts were synthesized by impregnation, freeze-drying and H_2 reduction. Typically, hNCNC was dispersed in an aqueous solution containing appropriate amount of $H_2PtCl_6 \cdot H_2O$. The mixture was stirred at 70 ℃ for 10 h, then freeze-dried for 24 h. The resulting powder was then reduced in H_2 atmosphere at 300 ℃ for 2 h, leading to the Pt/hNCNC. Pt/hCNC, Pt/cNCNC and Pt/CB were prepared by a similar impregnation and H_2 reduction process. The Pt mass loading is 4 wt.% for all the catalysts.

Characterization

The composition of the samples was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer, Avio500), X-ray photoelectron spectroscopy (XPS, ULVAC-PHI INC, PHI 5000 VersaProbe, Al K_α). The binding energies of XPS spectra refer to C 1s at 284.6 eV. The morphology and structure of the samples were characterized by X-ray diffraction (XRD, Philips X'pert Pro X-ray diffractometer), and high-resolution transmission electron microscopy (HRTEM, JEOL-JEM-2100). N_2 adsorption/desorption isotherms were measured on Thermo Fisher Scientific Surfer Gas Adsorption Porosimeter at 77 K after degassed at 300 °C for 6 h. The specific surface area and pore size distribution were calculated by the Brunauer-Emmett-Teller (BET, $0.05<p/p_0<0.3$), Horvath-Kawazoe (HK, <2 nm micropores) and Barrett-Joyner-Halenda (BJH, >2 nm mesopores and macropores) methods from the adsorption branch data, respectively.

CO temperature-programmed desorption (CO-TPD) measurements were conducted by using 50 mg sample pre-reduced in H_2 flow at 300 °C for 2 h. After the adsorption of CO for 30 min, the temperature was elevated to 400 °C with a rate of 10 °C min^{-1}, and the desorbed CO was detected by on-line mass spectrometry.

Activity measurements

Preferential oxidation of CO in H_2 experiments were performed in a continuous flow fixed-bed quartz-glass microreactor (i.d. =6 nm) at atmospheric pressure. 20 mg of catalyst was mixed with 1.0 g of quartz sand (40-60 mesh). All the catalysts were *in situ* reduced for 120 min in H_2 at 300 °C before the catalytic test. The reaction gas mixture consists of 1 vol.% CO, 1 vol.% O_2, 49 vol.% H_2 and N_2. The weight hourly space velocity (WHSV) of total gaseous reactant was 24,000 mL g^{-1} h^{-1} . The reactants and products were analyzed by gas chromatography (GC, Qiyang GC9860), using a 5A molecular sieve column (2 m, 3 mm) connecting to a flame ionization detector. The CO conversion and the CO_2 selectivity are calculated as follows:

$$CO\ conversion(\%) = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100$$

$$\mathrm{CO_2\ selectivity}(\%) = \left\{0.5 \times \frac{[\mathrm{CO}]_{in} - [\mathrm{CO}]_{out}}{[O_2]_{in} - [O_2]_{out}}\right\} \times 100$$

For kinetic measurement, the sample was diluted with quartz sand in a weight ratio of 1/30 and the performance was detected at a relatively high space velocity to ensure the conversions of all reactants below 20 %. The CO conversions (X_{CO}) were used to calculate the CO oxidation rates ($mol_{CO}\ g_{Pt}^{-1}\ h^{-1}$):

$$r_{CO} = \frac{X_{CO} \cdot N_{CO}}{m_{Pt}}$$

Where m_{Pt} was the mass of Pt in the reactor bed, N_{CO} was CO molar flow rate in mol h^{-1}.

Mass flows of CO (99.9%), H_2 (99.999%), O_2 (99.999%), N_2 (99.999%, internal standard), and CO_2 (99.99%) were controlled by mass flow controllers (STEC).

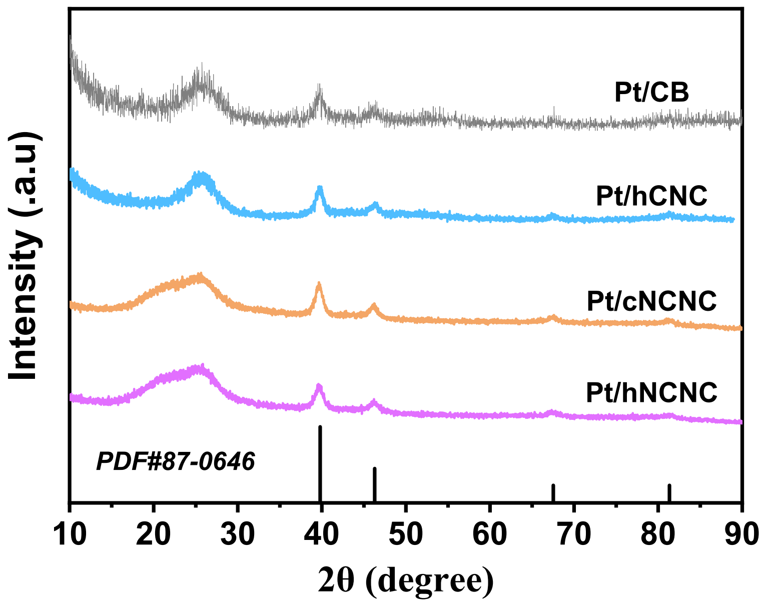

Figure S1. XRD patterns of Pt/CB, Pt/hCNC, Pt/cNCNC and Pt/hNCNC.

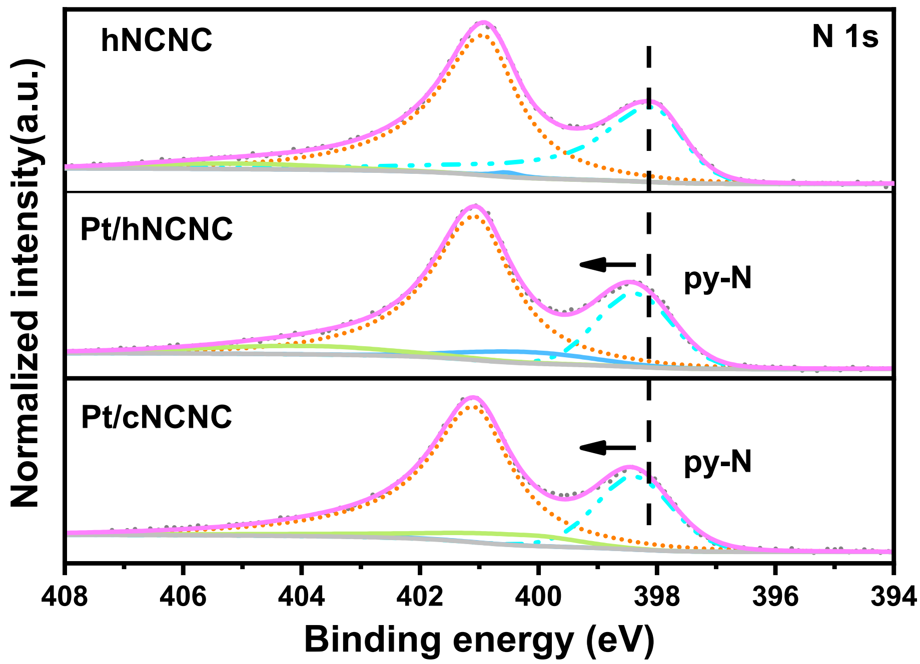

Figure S2. N 1s XPS spectra of hNCNC, Pt/hNCNC and Pt/cNCNC.

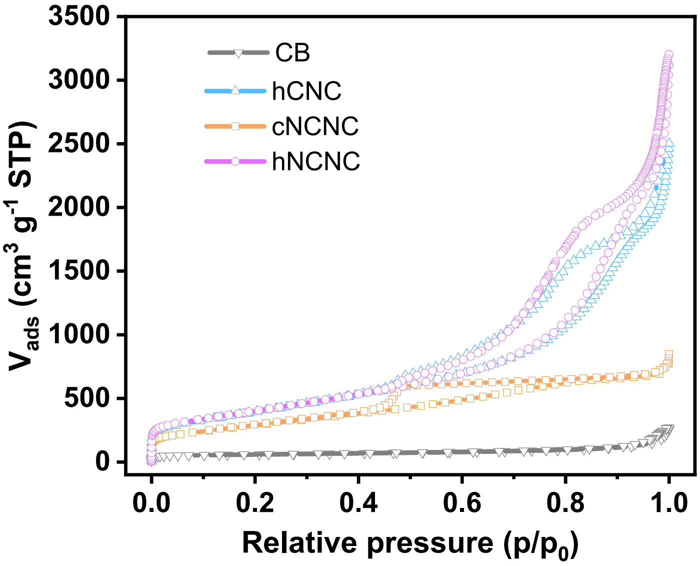

Figure S3. N_2 adsorption-desorption isotherms of CB, hCNC, cNCNC, and hNCNC.

The specific surface areas (SSA) of CB, hCNC, cNCNC, and hNCNC are 208.28 m^2 g^{-1}, 1050.6 m^2 g^{-1}, 1441.5 m^2 g^{-1}, 1447.3 m^2 g^{-1}, respectively.

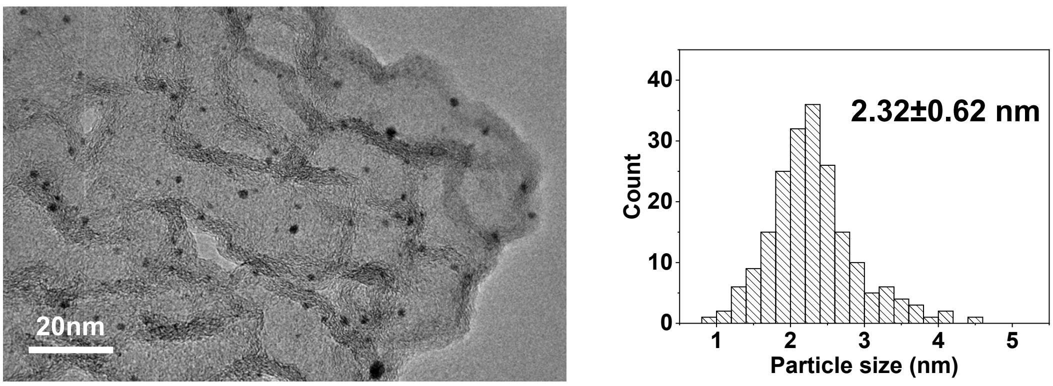

Figure S4. TEM image and corresponding Pt particle size distribution of Pt/hNCNC after the stability test at 180 °C for 100 h.

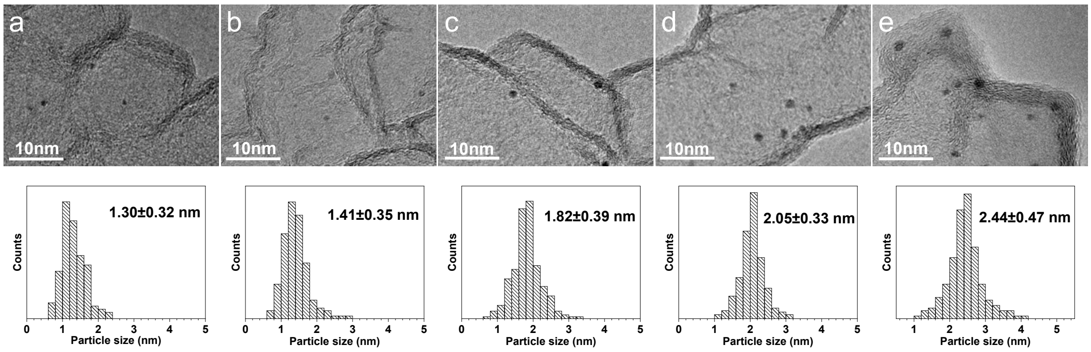

Figure S5. TEM images and Pt particle size distributions of Pt/hNCNC catalysts with different Pt loadings. (a) 1 wt.%, (b) 2 wt.%, (c) 3 wt.%, (d) 4 wt.%, (e) 6 wt.%.

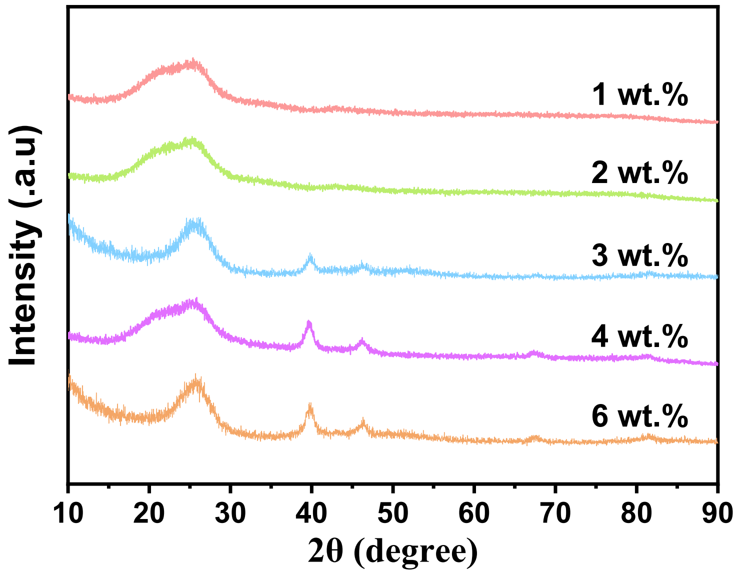

Figure S6. XRD patterns of Pt/hNCNC catalysts with different Pt loadings.

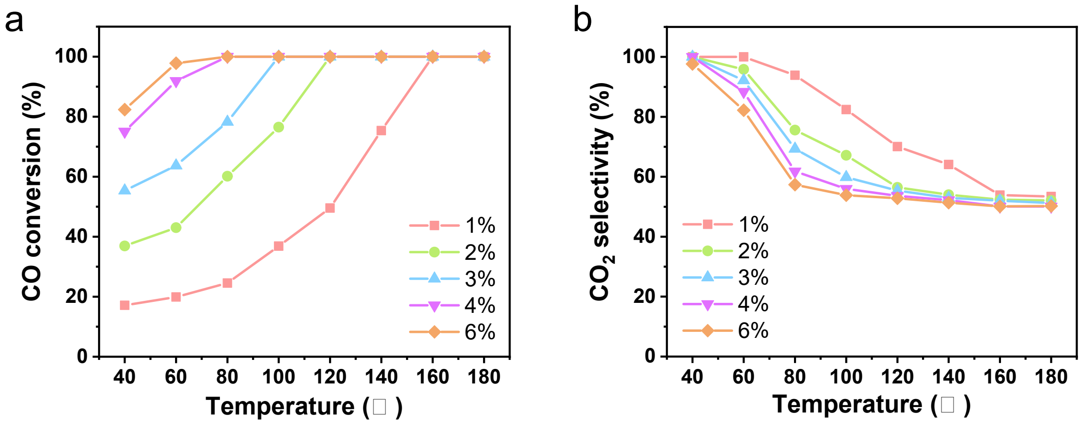

Figure S7. PROX performances of Pt/hNCNC catalysts with different Pt loadings. (a) CO conversion, (b) CO selectivity. Conditions: 1% CO, 1% O_2 and 49% H_2 balanced in nitrogen; space velocity: 24,000 mL g^{-1} h^{-1}; 0.1 MPa.

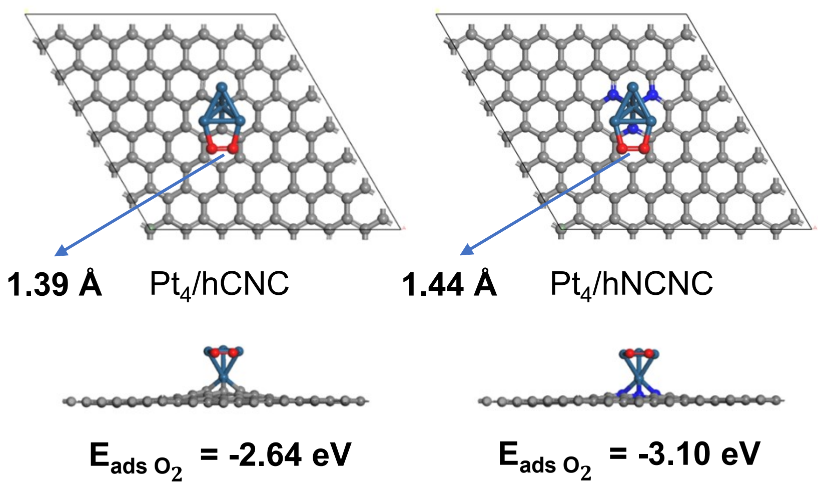

Figure S8. The modes for the adsorption of an O_2 molecule on Pt_4/hCNC and Pt_4/hNCNC.

Table S1. The Pt loading of Pt/CB, Pt/hCNC, Pt/cNCNC, and Pt/hNCNC analyzed by ICP-OES.

Sample	Pt/CB	Pt/hCNC	Pt/cNCNC	Pt/hNCNC
Pt (wt.%)	3.99	3.98	4.01	3.99

Table S2. Comparison of the PROX performances.

Catalysts	Pt loadings (wt%)	Composition of feed gas (%)			Space velocity (mL h^{-1} g_{cat}^{-1})	Maximal CO conversion (%)	Temperature window for the maximal CO conversion (°C)	ΔT(°C)	Ref
		CO	O_2	H_2					
Pt/hNCNC	1	1	1	49	24000	100	160-180	20	This work
	2	1	1	49	24000	100	120-180	60	
	4	1	1	49	24000	100	80-180	100	
Pt/cNCNC	4	1	1	49	24000	100	120-180	60	
Pt/hCNC	4	1	1	49	24000	100	120-180	60	
Pt/CNT	4	1	1	50	120000	100	170	0	3
Pt/CNT	3	1	0.5	98.5	25000	80	100	0	4
Pt/CB	2	1	0.5	98.5	25000	~60	180	0	5
Pt/CNT	1	2	2	20	30000	100	180	0	6
Pt/AC	1	2	1	20	30000	50	180	0	
Pt/SiO_2	3.6	1	0.5	48	36000	~80	~154-200	46	7
Pt/SiO_2	1	0.5	0.5	45	120000	95	227	0	8
Pt/SiO_2	4	1	0.5	98.5	36000	70	200	0	9
Pt/Mesoporous Silica	5	1	1	93	12000	100	~150	0	10
	5	1	0.5	93.5	12000	100	~60-150	90	
Pt/TiO_2	1	0.5	0.5	45	120000	75	250	0	11
Pt/γ-Al_2O_3	1	0.5	0.5	45	120000	100	~200	0	
Pt/γ-Al_2O_3	1	1	1	10	60000	100	~177	0	12
	1	1	1	80	60000	70	~202	0	
Pt/Al_2O_3	0.72	1	1	50	20000	~73	200	0	13

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