

Pd-loaded unique urchin-structured Ga₂O₃ for selective CO₂ photoreduction to CH₄

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Experimental section

Chemicals. Gallium nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, $\geq 99.9\%$), Palladium nitrate dihydrate ($\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$), Hexyl alcohol ($\text{CH}_3(\text{CH}_2)_5\text{OH}$, $\geq 99\%$), Dodecane ($\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$, $\geq 99\%$), Diethylene glycol ($(\text{HOCH}_2\text{CH}_2)_2\text{O}$, $\geq 99\%$), NaBH_4 ($\geq 99\%$), Ammonia hydroxide solution (AR), and Hexadecyltrimethyl ammonium bromide (CTAB, $\geq 99\%$). All the chemicals were purchased from Innochem Technology Co., Ltd. (Beijing, China) and used without further purification.

Synthesis of $\beta\text{-Ga}_2\text{O}_3$. Dissolved 0.612 g of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ in 3 g of deionized water and stirred thoroughly to obtain a gallium nitrate aqueous solution. Then mixed the prepared gallium nitrate solution with 25 mL dodecane, 2.28 g CTAB, and 2.5 mL hexyl alcohol and stirred for 1 hour to obtain mixture A. Mixed 3.612 g of ammonia solution, 25 mL of dodecane, 2.28 g of CTAB, and 2.5 mL of hexyl alcohol and stirred for 1 hour to obtain mixture B. Added mixture B dropwise to mixture A to adjust the pH to 9. Subsequently, an aging reaction was carried out at temperatures of 50, 70, and 90 °C, with an aging time of 9 hours. When the water bath was cooled to room temperature, 80 mL of diethylene glycol was added to the mixed solution. After filtration and washing, the resulting white precipitate was calcined at 900 °C for 3 hours. The calcined products were labeled as $\text{Ga}_2\text{O}_3\text{-50}$, $\text{Ga}_2\text{O}_3\text{-70}$, and $\text{Ga}_2\text{O}_3\text{-90}$, respectively.

Synthesis of Pd-loaded $\beta\text{-Ga}_2\text{O}_3$. Typically, dissolved 1 g of $\text{Ga}_2\text{O}_3\text{-90}$ powder in 50 mL of deionized water and sonicated for 30 minutes, then added a certain amount of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ to the solution and continued stirring for 1 hour to obtain 1wt%,

2wt%, 3wt%, and 5wt% Pd²⁺ solution. Subsequently, NaBH₄ was added to the solution to reduce Pd²⁺ to Pd⁰. After filtration and washing, the precipitate was collected and dried in a 60 °C vacuum drying oven for 24 hours. Ga₂O₃-90 with Pd loadings of 1%, 2%, 3%, and 5% were labeled as 1%Pd/ Ga₂O₃-90, 2%Pd/ Ga₂O₃-90, 3%Pd/ Ga₂O₃-90, and 5%Pd/ Ga₂O₃-90.

Characterization.

The crystal structure of the samples was determined by X-ray diffraction (XRD, Rigaku Ultima III, Rigaku Corporation, Japan). The microstructure and elemental composition were analyzed by field emission scanning electron microscopy (FE-SEM, ZEISS SIGMA 500 FE-SEM, Carl Zeiss AG, Germany) and transmission electron microscopy (TEM, Talos F200S, Thermo Fisher Scientific, U.S.A). The surface chemical composition and chemical bond vibration were characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, U.S.A) and Fourier-transform infrared (FTIR, Nicolet 6700, Thermo Fisher Scientific, U.S.A). Electron paramagnetic spectroscopy (EPR, Bruker EMXplus, Germany) was performed to characterize the oxygen vacancies in the photocatalysts. Nitrogen adsorption-desorption isotherms were obtained on an ASAP 2020 adsorption analyzer supplied by Micromeritics (ASAP 2020HD88, Micromeritics, U.S.A). The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were obtained from a UV-vis spectrophotometer (PerkinElmer Lambda 75, PerkinElmer, U.S.A). Photoluminescence (PL) spectra were collected by the fluorescence spectrometers (Edinburgh FLS980, Edinburgh Instruments, Britain) with an emission wavelength of

280 nm.

Photoelectrochemical measurements. 5 mg as-prepared photocatalyst was uniformly dispersed in a 40 μ L mixed solution (Nafion:ethanol=1:1). Then, the suspension was coated on a 1 cm \times 2 cm indium tin oxide (ITO) glass and dried for 3 hours at a temperature of 50 $^{\circ}$ C. The photoelectrochemical performance was measured by an electrochemical workstation (Chi662D, Shanghai Chenhua, China) with a three-electrode cell. ITO glass, Pt foil and Ag/AgCl were used as the working electrode, counter electrode, and reference electrode, respectively. Moreover, the light source was a 300 W mercury lamp (CELHXF300, Beijing China education Au-light, China) with a power density of 100 mW/cm².

Photocatalytic CO₂ reduction measurements. 15 mg of photocatalyst was uniformly dispersed in a 100 mL reactor containing 5 mL of water. Before the CO₂ reduction reaction begins, continuously introduced high purity CO₂ into the reactor for 40 minutes. Then a 300 W mercury lamp was used as the irradiation source to excite the photogenerated electrons of the catalyst. The entire photocatalytic reduction of CO₂ reaction lasted for 8 hours, and 1 mL of gas was extracted from the glass chamber every hour interval to detect. The species and amount of the product were analyzed by gas chromatography (GC-7920-TF2A, Beijing China education Au-light, China) with Ar as the carrier gas. CH₄ was first reduced to CO in the methane reactor, and then the amount of CO was detected by a flame ionization detector (FID) to determine the amount of CH₄ produced during the photocatalytic reaction process. The selectivity of CH₄ was calculated using the following equation:

$$S_{CH_4} = \frac{Y_{CH_4} \times 8}{Y_{CH_4} \times 8 + Y_{CO} \times 2}$$

Where S_{CH_4} represents the selectivity of CH_4 , Y_{CH_4} and Y_{CO} represents the yields of CH_4 and CO , respectively. The cyclic experiment was conducted with 15 mg catalyst, and after the CO_2 reduction reaction was completed, CO_2 was refilled again for the reaction. This process was repeated 8 times. The C source for isotope labeling experiments was detected by gaschromatography–mass spectrometry (GC-MS, 7890A and 5975C, Agilent, U.S.A).

In situ DRIFTS measurements. The in-situ DRIFTS spectra were collected from a FTIR spectrometer (INVENIO S, Bruker, Germany). Typically, Placed the sample in the reaction chamber and raised temperature to 200 °C and blew the sample with Ar. Collected background baseline after the reaction chamber had cooled to room temperature. Subsequently, CO_2 and H_2O were introduced under dark conditions, and after adsorption saturation, light was turned on. The data of the spectra were collected at 10, 20, 30, 40, and 50 minutes, respectively.

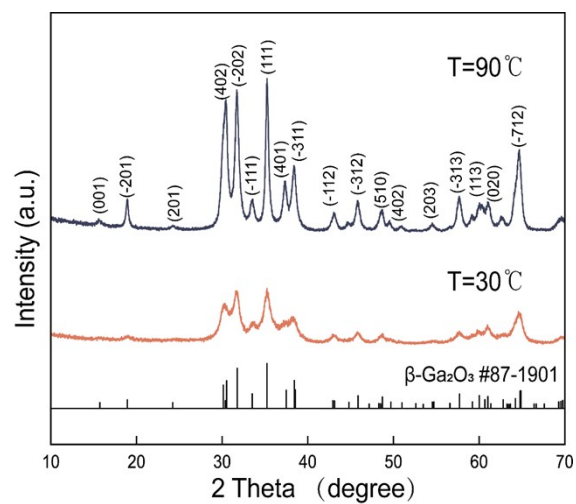


Fig. S1 XRD patterns of Ga_2O_3 synthesized at aging temperatures of 30 and 90°C.

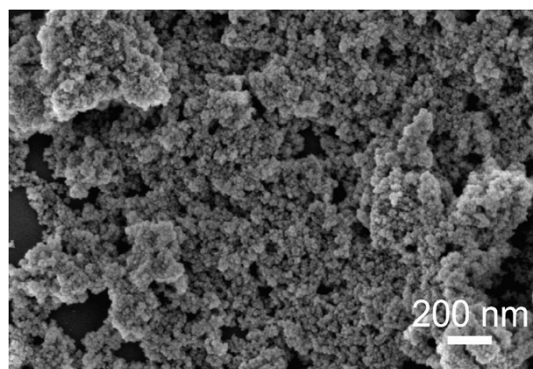


Fig. S2 SEM image of Ga₂O₃ synthesized at an aging temperature of 30°C.

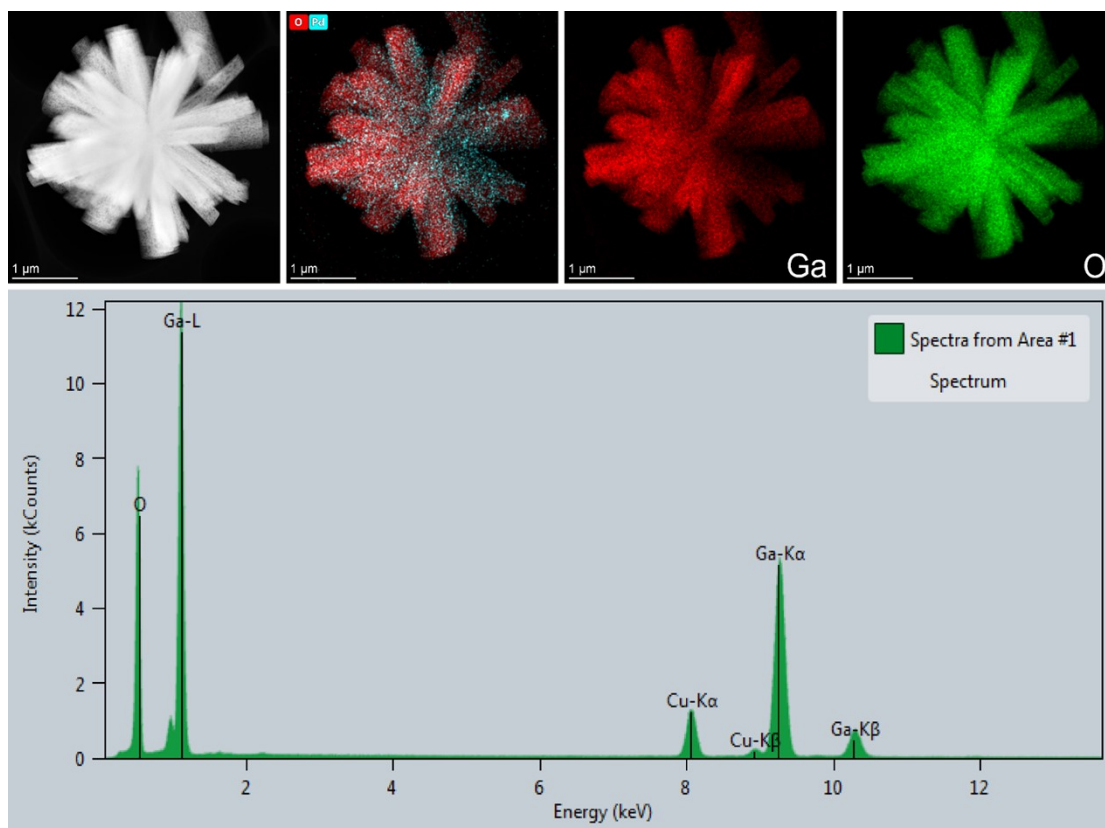


Fig. S3 EDS spectra and elemental mapping of Ga₂O₃-90.

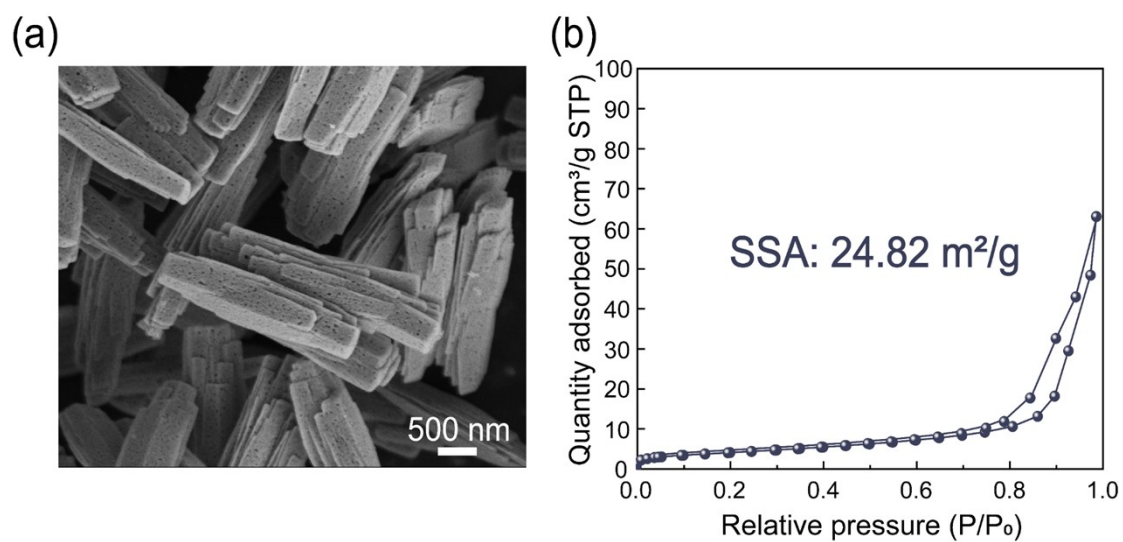


Fig. S4 (a) SEM image of Ga₂O₃ prepared at 100 °C; (b) N₂ adsorption–desorption isotherms of Ga₂O₃ prepared at 100 °C.

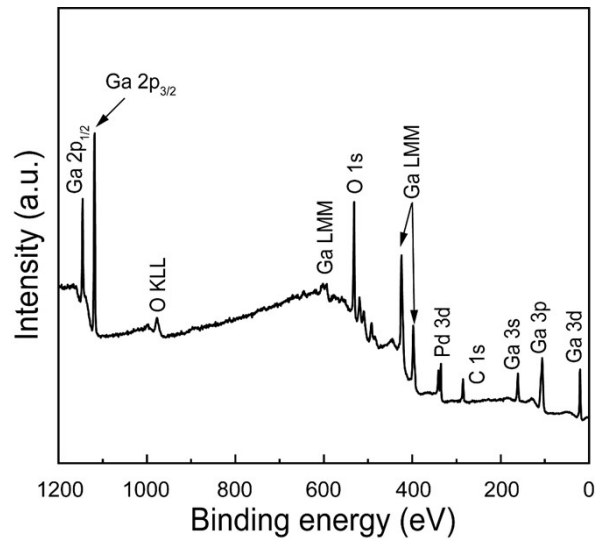


Fig. S5 XPS survey spectra of 2%Pd/Ga₂O₃-90.

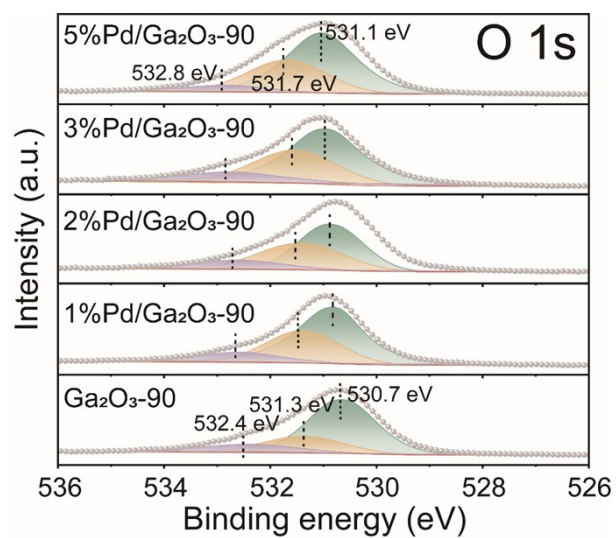


Fig. S6 O 1s spectrum of the as-prepared samples.

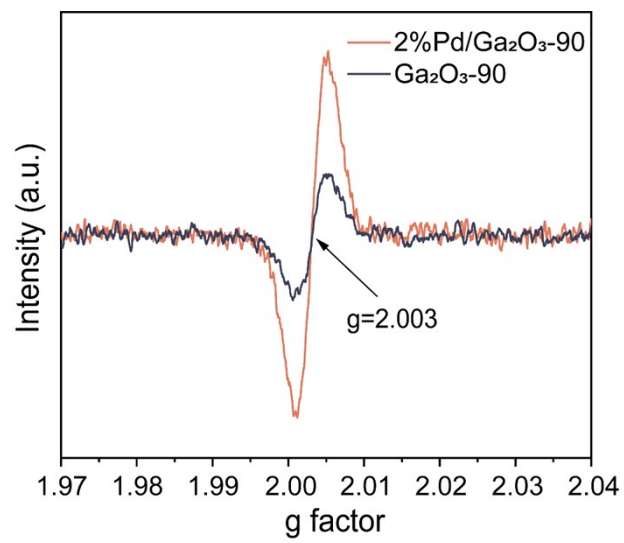


Fig. S7 EPR spectra of Ga₂O₃-90 and 2%Pd/Ga₂O₃-90.

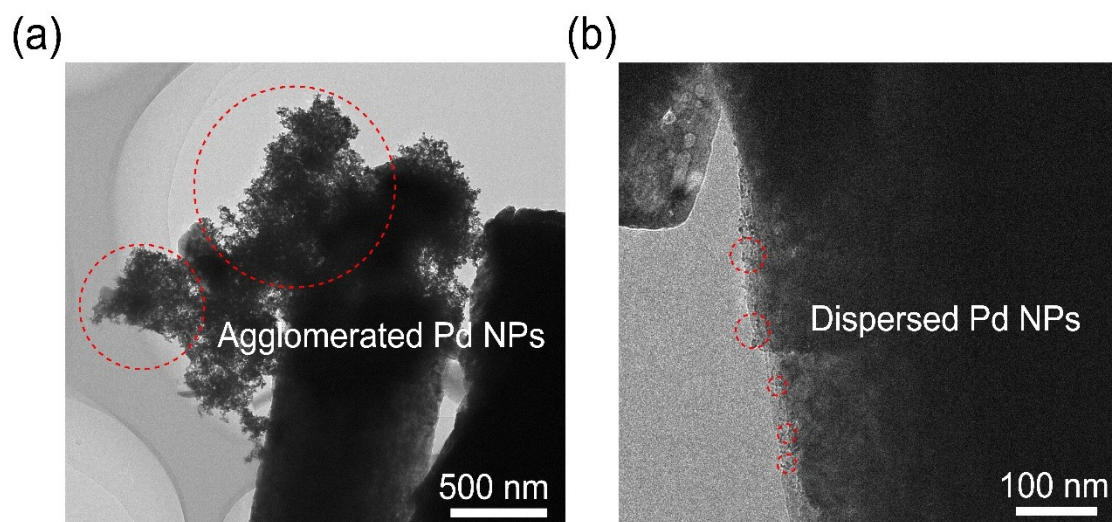


Fig. S8 TEM images of (a) 5%Pd/Ga₂O₃-90; (b) 2%Pd/Ga₂O₃-90.

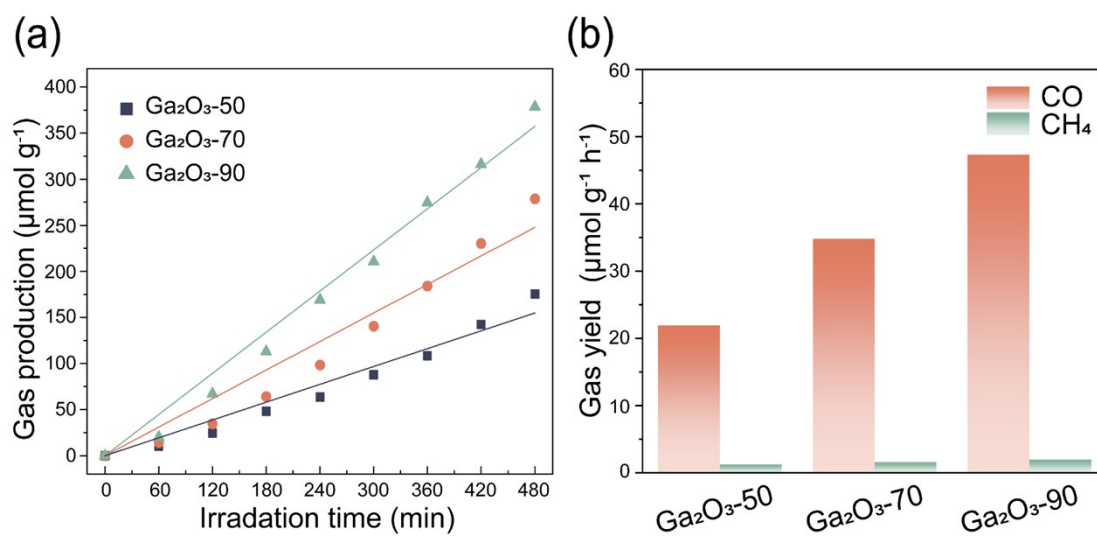


Fig. S9 (a) CO production of different catalysts; (b) Yield of CO and CH₄ from different catalysts.

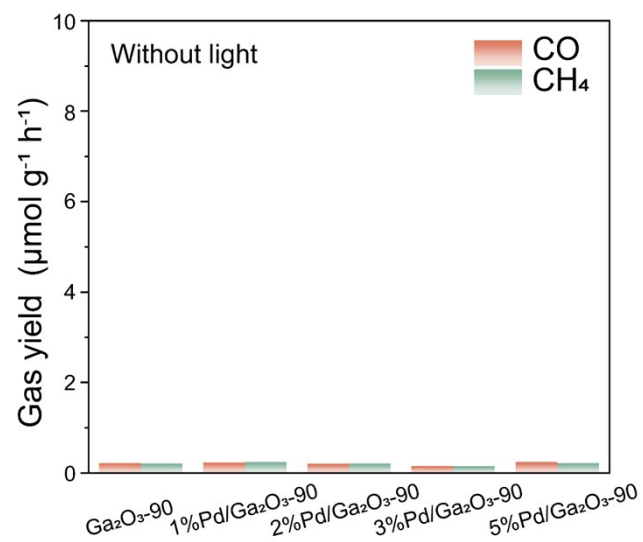


Fig. S10 CO and CH₄ yield of different catalysts under dark condition.

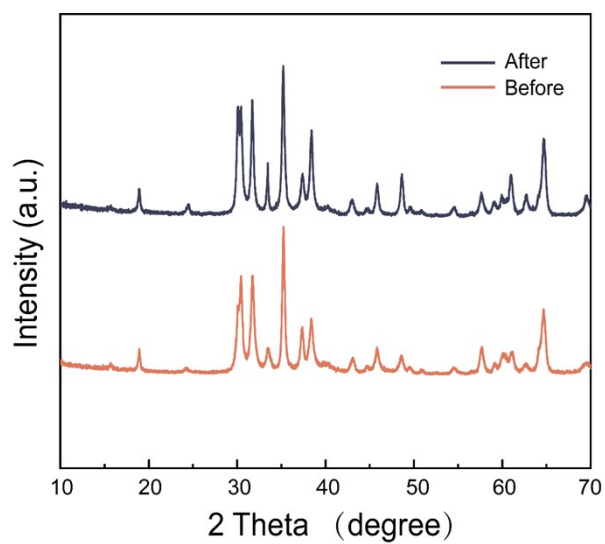


Fig. S11 XRD patterns of 2%Pd/Ga₂O₃-90 before and after reaction.

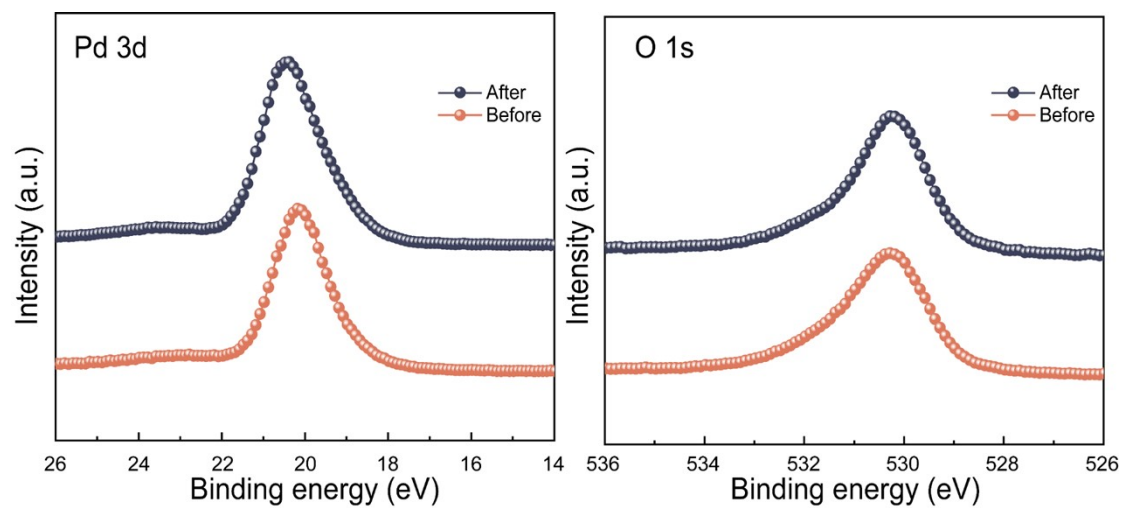


Fig. S12 XPS spectra of 2%Pd/Ga₂O₃-90 before and after reaction.

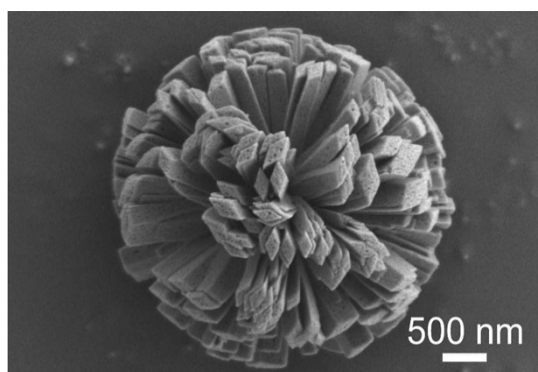


Fig. S13 SEM image of 2%Pd/Ga₂O₃-90 after reaction.

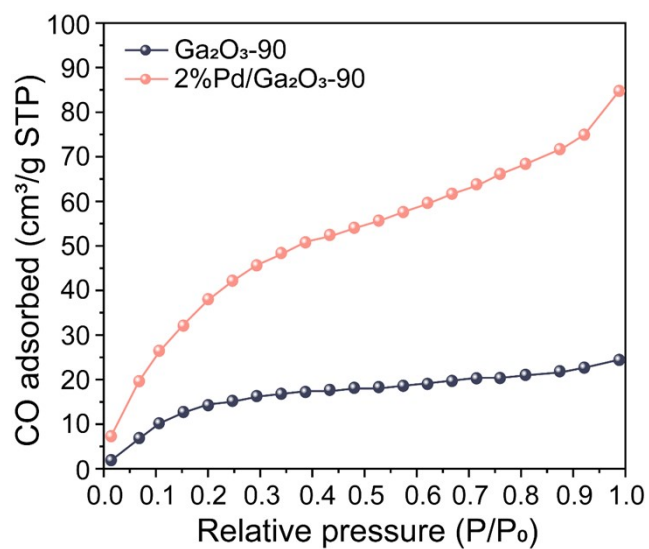


Fig S14 CO adsorption isotherms of Ga₂O₃-90 and 2%Pd/Ga₂O₃-90.

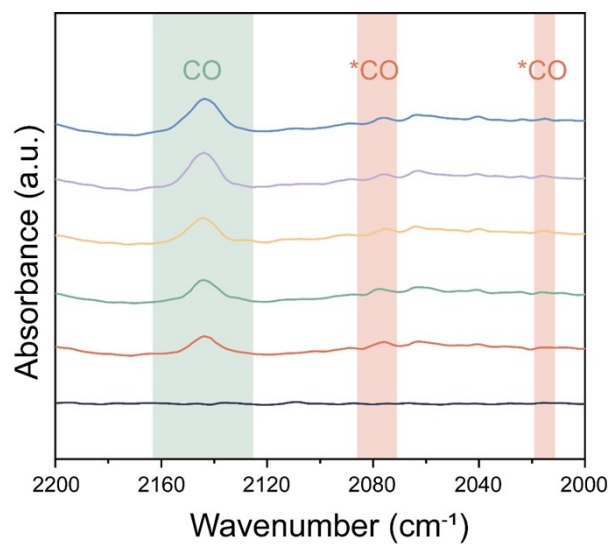


Fig S15 In situ DRIFTS spectra of Ga₂O₃-90 within the range of 2000-2200 cm⁻¹.

Table S1 BET surface area of Ga₂O₃-50, Ga₂O₃-70, and Ga₂O₃-90.

Sample	Ga ₂ O ₃ -50	Ga ₂ O ₃ -70	Ga ₂ O ₃ -90
Specific surface area (m ² /g)	22.4	32.8	44.7

Table S2 Fitting results of τ_1 and τ_2 for the decay curves under a 260 nm excitation (ns).

Sample	A_1	A_2	τ_1	τ_2	Average lifetime
Ga ₂ O ₃ -90	808.9095	210.1370	0.9984	7.2251	2.107
1%Pd/Ga ₂ O ₃ -90	933.6121	216.1265	0.9246	3.7483	3.462
2%Pd/Ga ₂ O ₃ -90	779.1401	259.1584	0.7769	3.1076	5.062
3%Pd/Ga ₂ O ₃ -90	883.2717	249.1115	1.0928	4.8018	3.145
5%Pd/Ga ₂ O ₃ -90	766.2424	208.8765	0.9103	5.1202	2.297