Electronic Supplementary Information (ESI)

Synergism of surface strain and interfacial polarization on Pd@Au core-shell cocatalysts for highly efficient photocatalytic CO₂ reduction over TiO₂

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Additional experimental

Chemicals. K_2PdCl_4 (Aladdin, P106044), poly(vinyl pyrrolidone) (PVP, M.W.~55000, Aldrich, 856568), 3-mercaptopropionic acid (MPA, Aldrich, M5801) were used in the synthesis. All other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All the chemicals were used as received without further purification. The deionized water used in all experiments was prepared by passing through an ultra-pure purification system.

Synthesis of TiO_2 nanosheets. The TiO_2 nanosheets were synthesized by modifying a method reported in the literature using hydrofluoric acid as a capping agent.^{S1} Caution! Hydrofluoric acid is extremely corrosive and toxic and should be handled with extreme care.

Synthesis of TiO₂-Pd. In a typical synthesis of TiO₂-Pd, PVP (MW \approx 55,000, 105 mg), ascorbic acid (60 mg) and KBr (300 mg) were dissolved in 8 mL of water containing 160 mg of TiO₂ nanosheets. The reaction mixture was transferred into a 50-mL three-neck flask, which was then pre-heated under magnetic stirring at 80 °C for 10 min. Subsequently, 3.0 mL of aqueous solution containing K₂PdCl₄ (32.0 mg) was added into the flask, and the reaction was allowed to proceed at 80 °C for 3 h. The product was collected via centrifugation, washed with water for four times, and dried at 45 °C in a vacuum.

Synthesis of TiO₂-Au. TiO₂-Au was synthesized with the deposition of presynthesized Au nanocubes onto the TiO₂ nanosheets. In a typical synthesis of Au nanocubes.^{S2} Au seeds were firstly prepared by mixing an ice-cold aqueous solution of NaBH₄ solution (0.6 mL, 10 mM) with an aqueous HAuCl₄·4H₂O solution (0.25 mL, 10 mM) and an aqueous cetyltrimethylammonium bromide (CTAB) solution (7.5 mL, 100 mM). After 2 min rigorous stirring, the mixture was left undisturbed at room temperature for 1 h. Then the CTAB-stabilized seed solution was diluted 10

During the preparation of the growth solution, aqueous times with water. HAuCl₄·4H₂O (0.8 mL, 10 mM), aqueous solution of cetyltrimethylammonium bromide (CTAB) (6.4 mL, 100 mM) and aqueous ascorbic acid (3.8 mL, 100 mM) were mixed into water (32 mL) and then 20 µL diluted seed solution was added into the growth solution. Finally, the mixture was mildly stirred for 10 s and then left undisturbed at room temperature for 2 h. The product was collected by centrifugation at 10,000 rpm for 5 min, washed three times with water and redispersed in water. During the synthesis of TiO₂-Au, 20 mg of TiO₂ nanosheets were dispersed in 50 mL of water through sonication. Subsequently, 50 µL of $NH_3 H_2O$ (28%) and 50 µL of MPA were added into the mixture. Then, 1400 µL aqueous solution of Au nanocubes (1.64 mg mL⁻¹) was added under sonication for 10 min. The as-obtained mixture was kept static for precipitation, centrifuged and washed with water for four times, dried at 45 °C in a vacuum, and annealed at 150 °C for 2 h in Ar atomsphere to obtain the final product.

Sample characterization. Transmission electron microscopy (TEM), highresolution TEM (HRTEM) images, scanning TEM (STEM) images and energydispersive spectroscopy (EDS) mapping profiles were taken on a JEOL JEM-2100F field-emission high-resolution transmission electron microscope operated at 200 kV. The atomic-resolution high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) images were collected on a JEOL JEM-ARM200F TEM/STEM with a spherical aberration corrector working at 200 kV. Powder X-ray powder diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer with Non-monochromated Cu-Ka X-Ray. X-ray photoelectron spectra (XPS) were collected on an ESCALab 250 X-ray photoelectron spectrometer, using nonmonochromatized Al-Ka X-ray as the excitation source. UV-vis-NIR diffuse reflectance data were recorded in the spectral region of 200-800 nm with a Cary-7000 Series UV-Vis-NIR spectrophotometer. Photoluminescence (PL) spectra were recorded on a HITACHI F-7000 Spectrofluorometer.

Computational methods. Density functional theory calculations were performed by using the Vienna ab initio simulation package (VASP).^{S3,S4} The Perdew-Burke-Ernzerhof (PBE)^{S5} functional was adopted to treat the electron exchange and correlation effects by the generalized gradient approximation (GGA).^{S6} The projector augmented plane wave (PAW) method with a frozen-core approximation was used to describe electron-ion interaction.^{S7} The Brillouin zone integration was approximated by a sum over special k-points using the Monkhorst-Pack grids.^{S8} The Gaussian smearing method is used with a value of 0.1 eV.^{S9} The cutoff energy was set as 400 eV for the plane wave basis set. The Kohn-Sham equations were solved self-consistently. The energy tolerance was set to 1.0×10^{-6} eV; the maximum Hellmann Feynman force tolerance was set to 0.03 eV/Å for structure optimization.

A periodic 2 × 2 slab model with four layers of Au(100) is established with the vacuum space of 12 Å. The two bottom layers were fixed during the relaxation simulations.^{S10} The Brillouin zone integration was carried out with $2\times2\times1$ *k*-point sampling in DFT calculation. In free energy calculations, the entropic correlation and zero-point vibration energy have been included 0.45 eV was employed for the correction of electronic energy for CO₂ due to an overestimation by DFT formalism; and -0.2 eV was used for the *COOH to approximate water-induced stabilization in the present calculations.^{S11}

The transition state location of CO₂ reduction on Au(100) surfaces were calculated by the Double-Ended Surface Walking (DESW) method, a methodology of LASP package developed by Liu's Group.^{S12-S14} It is an unbiased general-purpose potential energy surface searching method for both the structure and pathway prediction of a complex system, which is based on the idea of bias-potential-driven dynamics and Metropolis Monte Carlo. The corresponding activation energies were calculated according to the energy difference between the initial and transition states. Frequency analysis was carried out to verify no imaginary frequency for the stable configurations and a single imaginary one for the transition state structure.



Fig. S1 Schematic illustrating the synthesis of TiO_2 -Pd@Au samples.



Fig. S2 TEM and HRTEM images of TiO_2 nanosheets: (a) TEM image showing the flat surface of nanosheets; (b) TEM image showing the cross section and thickness of a nanosheet; (c) HRTEM image taken from a flat face of nanosheet; (d) HRTEM image taken from a cross section of nanosheet.



Fig. S3 (a,b) TEM images of TiO_2 -Pd; (c) TEM image of TiO_2 -Pd with a standing-up TiO_2 nanosheet; (d) HRTEM image of TiO_2 -Pd.



Fig. S4 (a) Schematic illustrating the TiO₂-Au sample; (b,c) TEM images of TiO₂-Au;(d) HRTEM image of TiO₂-Au.



Fig. S5 Survey XPS spectra of TiO₂ based samples.



Fig. S6 TEM images of TiO₂-Pd@Au-1 after the photocatalytic cyclic process.



Fig. S7 (a) XRD patterns of TiO₂-Pd@Au-1 before and after photocatalytic cyclic process; (b-f) XPS spectra of TiO₂-Pd@Au-1 before and after photocatalytic cyclic process: (b) survey spectra, (c) Ti2p, (d) O1s, (e) Pd3d and (f) Au4f high-resolution spectra.



Fig. S8 Differential charge density by first-principles simulations for the Au(100) shells on Pd(100) substrates in neutral state. The Au shell thickness is altered from 1 to 4 layers. The olive and cyan colors represent increase and decrease in electron density, respectively.



Fig. S9 Bader charge analysis of Au(100) surface under different surface strains.



Fig. S10 Transition states of TS1 (top) and TS2 (bottom) on Au(100) surface under different surface strains.



Fig. S11 Energy profile of CO_2 reduction reaction on Au(100) surface under different surface strains.

			Average CO	Selectivity	
Semiconductor	Metal cocatalyst	Wavelength range of irradiation light	production	for CO	Ref.
			rate (μ mol g _{cat} -	production	
			¹ h ⁻¹)	(%)	
TiO ₂	Au	UV light	12.6	44.3	29
		$(320 < \lambda < 420 \text{ nm})$			
TiO ₂	Au	full spectrum	31.1	42.0	47
TiO ₂	Au	UV light + visible light	0.7	4.8	48
TiO ₂	Au	full spectrum	14.5	44.0	49
TiO ₂	Au	UV light + visible light	2.1	30.6	50
		$(320 < \lambda < 780 \text{ nm})$			
TiO ₂	Au	UV light + visible light	1.5	4.4	51
		$(320 < \lambda < 780 \text{ nm})$			
TiO ₂	Pd@Au	UV light	166.2	90.6	*
		$(320 < \lambda < 420 \text{ nm})$	100.5		

Table S1. Comparison of the photocatalytic activity of as-obtained TiO₂-Pd@Au-1 in

 CO production with those of previously reported Au cocatalysts supported by TiO₂.

* The photocatalytic activity of TiO₂-Pd@Au-1 reported by us.

	ΔG (eV)			
Reactions	0 %	-1.93 %	-4.35 %	
$CO_2 + H^+ + e^- + * \rightarrow *COOH$	0.55	0.49	0.42	
$*COOH + H^+ + e^- \rightarrow *CO + H_2O(g)$	-0.51	-0.55	-0.63	
$*CO \rightarrow CO + *$	0.15	0.25	0.41	

Table S2. Free energies of CO_2 reduction on Au(100) with different surface strains.

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