**Electronic Supplementary Information (ESI)** 

## Interface engineering on Janus Pd-Au heterojunction cocatalysts for selective photocatalytic reduction of CO<sub>2</sub> to CH<sub>4</sub>

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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) and poly vinyl alcohol (PVA, MW = 9000-10000, Aldrich, 360627) 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 water used in all experiments was de-ionized water prepared by passing through an ultra-pure purification system.

Synthesis of  $TiO_2$  nanosheets. The  $TiO_2$  nanosheets were synthesized by modifying a method in the literature with hydrofluoric acid as a capping agent.<sup>S1</sup> Caution! Hydrofluoric acid is extremely corrosive and toxic, and should be handled with extreme care.

Synthesis of TiO<sub>2</sub>-Au and TiO<sub>2</sub>-Pd/Au. TiO<sub>2</sub>-Au and TiO<sub>2</sub>-Pd/Au were synthesized with the self-assembly of pre-synthesized Au nanospheres onto the TiO<sub>2</sub> and TiO2-Pd, respectively. In a typical synthesis of Au nanospheres, S2 Au seeds were firstly prepared by mixing an ice-cold aqueous solution of NaBH<sub>4</sub> solution (0.6 mL, 10 mM) with an aqueous HAuCl<sub>4</sub> solution (5 mL, 0.25 mM) and an aqueous cetyltrimethylammonium bromide (CTAB) solution (5 mL, 100 mM). A brown solution formed immediately after the introduction of NaBH<sub>4</sub> and the mixture was left undisturbed at 24 °C for 3 h. During the synthesis of Au nanospheres, aqueous HAuCl<sub>4</sub>·4H<sub>2</sub>O (2 mL, 0.5 mM), aqueous solution of cetyltrimethylammonium chloride (CTAC) (2 mL, 200 mM) and aqueous AA (1.5 mL, 100 mM) were mixed in a glass vial (20 mL) and then 100  $\mu$ L initial seed was added into the glass vial. The reaction was allowed to proceed at 24 °C for 10 min. The product was collected by centrifugation at 14,000 rpm for 15 min, washed three times with water and redispersed in water. During the synthesis of TiO<sub>2</sub>-Au, 20 mg of TiO<sub>2</sub> nanosheets were dispersed in 50 mL of water through sonication. Subsequently, 50  $\mu$ L of  $NH_3 \cdot H_2O$  (28%) and 50 µL of MPA were added into the mixture. Then, 1400 µL aqueous solution of Au nanospheres (1.64 mg/mL) was added under sonication for 10 The as-obtained mixture was kept static for precipitation, centrifuged and min.

washed with water for four times, dried at 45 °C in a vacuum and annealed in air at 200 °C for 4 h. The TiO<sub>2</sub>-Pd/Au was synthesized under the same experimental conditions as TiO<sub>2</sub>-Au except for the use of TiO<sub>2</sub>-Pd instead of TiO<sub>2</sub> as a precursor.

Synthesis of TiO<sub>2</sub>-Pd@Au. In a typical synthesis of TiO<sub>2</sub>-Pd@Au, a solution was firstly prepared in a vial as follows: 9.625 mL aqueous solution containing 0.32 g cetyltrimethylammonium chloride (CTAC), 10  $\mu$ L aqueous solution of NaBr (0.01 M), 80  $\mu$ L aqueous solution of HAuCl<sub>4</sub> (10 mM) and 90  $\mu$ L aqueous solution of AA (0.04 M) were mixed at 30 °C to obtain a colorless solution. Subsequently, 1.3 mg of TiO<sub>2</sub>-Pd was added into the mixed solution. The solution in the vial was left undisturbed for 15 min to complete the Au growth. The resultant product was separated by centrifugation, washed with water for four times, and dried at 45 °C in a vacuum.

**Synthesis of TiO<sub>2</sub>-Au@Pd.** In a typical synthesis of TiO<sub>2</sub>-Au@Pd, 20 mg of TiO<sub>2</sub>-Au was mixed with an aqueous solution of CTAB (8.85 mL, 0.1 M), followed by the addition of K<sub>2</sub>PdCl<sub>4</sub> (1150  $\mu$ L, 10 mM) and HCl (100  $\mu$ L, 1 M) aqueous solutions. Subsequently, a aqueous solution of AA (460  $\mu$ L, 0.1 M) was added into the mixture, which was then shaken and kept in an oil bath at 50 °C for 2 h. Finally, the products were centrifuged and washed with water for four times, and dried at 45 °C in a vacuum.

**Synthesis of TiO<sub>2</sub>-PdAu.** In a typical synthesis of TiO<sub>2</sub>-PdAu, 1.5 mL aqueous solution of HAuCl<sub>4</sub> (10 mM) and 1.5 mL aqueous solution of K<sub>2</sub>PdCl<sub>4</sub> (10 mM), 550  $\mu$ L aqueous solution of poly vinyl alcohol (PVA) (1 wt%) and 20 mg of TiO<sub>2</sub> were mixed with 50 mL deionized water to form homogeneous suspension under continuous stirring. Then 1.5 mL of fresh aqueous solution of NaBH<sub>4</sub> (0.1 M) was added. After stirring for 2 h at room temperature, the product were centrifuged and washed with water for four times, and dried at 45 °C in a vacuum.

**Synthesis of TiO<sub>2</sub>-PdH<sub>0.43</sub>-Au.** In a typical synthesis of TiO<sub>2</sub>-PdH<sub>0.43</sub>-Au, 20 mg of the TiO<sub>2</sub>-Pd-Au was re-dispersed in 10 mL of N,N-dimethylformamide (DMF) in a 20 mL Teflon-lined stainless-steel autoclave, which was then heated at 160 °C for 16 h.

The product was separated via centrifugation, washed with water for four times, and dried at 45 °C in a vacuum.

Sample characterizations. 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. Powder X-ray powder diffraction (XRD) patterns were collected on a D8 Advance Xray 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-K $\alpha$  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. The loading amounts of metal on the TiO<sub>2</sub> nanosheets were determined by sample weighing prior to the dissolution of metal for the ICP-MS measurements. The concentrations of Pd and Au were measured as follows: the samples were dissolved with a mixture of  $HNO_3$ and HCl (1 : 3, volume ratio), which was then diluted with 1% HNO<sub>3</sub>. The concentrations of metal ions were then measured through a Thermo Scientific PlasmaQuad 3 inductively-coupled plasma mass spectrometry (ICP-MS).

**Photoelectrochemical measurements.** 3.0 mg as-synthesized products were dispersed in a mixture of 10  $\mu$ L ethanol and 10  $\mu$ L Nafion, which were then uniformly spin-dropped onto at a 1 cm  $\times$  1 cm indium tin oxide (ITO)-coated glass by a spin coater (SC-1B, China). Subsequently, the ITO-coated glasses were heated at 80 °C in a vacuum oven for 1 h. The photocurrents were measured on a CHI 760E electrochemical station (Shanghai Chenhua, China) in ambient conditions under irradiation of a 300 W Xe lamp (Solaredge 700, China). UV light was used as the illumination source, which was realized in the presence of a short-wave-pass 420 nm ( $\lambda < 420$  nm) cutoff filter. The power density of the light was measured to be 2.7 mW cm<sup>-2</sup>. A three-electrode cell was used to perform the electrochemical

measurements. The working electrode was the ITO-coated glass. A Ag/AgCl electrode and Pt foil were used as the reference electrode and counter electrode, respectively. The three electrodes were inserted in a quartz cell filled with 0.5 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. The photoresponse of the prepared photoelectrodes (i.e., I-t) was operated by measuring the photocurrent density under chopped light irradiation (light on/off cycles: 60 s) at a bias potential of 0.4 V *vs*. Ag/AgCl for 400 s. Electrochemical impedance spectroscopy (EIS) was performed in the 10<sup>-1</sup> to 10<sup>5</sup> Hz frequency range with an AC voltage amplitude of 10 mV at an applied potential of 0.4 V *vs*. Ag/AgCl.

**Apparent quantum efficiency measurements.** The apparent quantum efficiency (AQE) was measured under the same photocatalytic reaction condition, except for the use of a 365 nm band-pass filter instead of a 420-nm cutoff filter. The AQE was calculated according to the following Equation:

 $AQE = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$ 

 $=\frac{\text{number of H}_2 \text{ molecules} \times 2 + \text{number of CO molecules} \times 2 + \text{number of CH}_4 \text{ molecules} \times 8}{\text{number of incident photons}} \times 100\%$ 



**Fig. S1** (a,b) TEM and (c,d) 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. S2 TEM images of  $TiO_2$ -Pd: (a) low-magnification TEM image and (b) TEM image with a standing-up  $TiO_2$  nanosheet.



**Fig. S3** (a) Low-magnified TEM image of  $TiO_2$ -Pd-Au; (b) TEM image and corresponding illustration of  $TiO_2$ -Pd-Au showing the Au deposited on two faces (1), around the edge (2) and corner (3); (c) TEM image and corresponding illustration of  $TiO_2$ -Pd-Au with a standing-up  $TiO_2$  nanosheet.



Fig. S4 TEM image of Pd-Au heterojunctions prepared under the same experimental conditions as  $TiO_2$ -Pd-Au except the use of Pd instead of  $TiO_2$ -Pd.



Fig. S5 Low-magnification TEM images of (a)  $TiO_2$ -Au, (b)  $TiO_2$ -Pd/Au, (c)  $TiO_2$ -Pd@Au and (d)  $TiO_2$ -Au@Pd.



Fig. S6 (a) TEM image and (b) corresponding illustration of  $TiO_2$ -Pd@Au with a standing-up  $TiO_2$  nanosheet; (c) TEM image and (d) corresponding illustration of  $TiO_2$ -Au@Pd with a standing-up  $TiO_2$  nanosheet.



Fig. S7 TEM images of  $TiO_2$ -Pd-Au after the photocatalytic cyclic process.



**Fig. S8** (a) XRD of TiO<sub>2</sub>-Pd-Au before and after the photocatalytic cyclic process; (bf) XPS spectra of TiO<sub>2</sub>-Pd-Au before and after the photocatalytic cyclic process: (b) survey spectra, (c) Ti2p, (d) O1s, (e) Pd3d and (f) Au4f high-resolution spectra.



Fig. S9 (a) Pd3d XPS spectrum of  $TiO_2$ -Pd@Au; (b) Au4f XPS spectrum of  $TiO_2$ -Au@Pd.



**Fig. S10** (a) Ti2p and (b) O1s XPS spectra over TiO<sub>2</sub>, TiO<sub>2</sub>-Pd, TiO<sub>2</sub>-Au, TiO<sub>2</sub>-Pd-Au, TiO<sub>2</sub>-Pd/Au, TiO<sub>2</sub>-Pd@Au, TiO<sub>2</sub>-Au@Pd and TiO<sub>2</sub>-PdAu. The peaks with binding energies of 459.0 eV and 464.7 eV in the high-resolution spectra of Ti2p are attributed to the Ti2p<sub>3/2</sub> and Ti2p<sub>1/2</sub>, respectively (Fig. S10a), while the peaks located at 530.0 eV and 531.6 eV in the O1s high-resolution spectra are assigned to O–Ti of TiO<sub>2</sub> and O–H of adsorbed OH groups on the TiO<sub>2</sub> surface (Fig. S10b).<sup>S3</sup> It can be clearly seen that there is no obvious change in the position of Ti2p and O1s peaks between the TiO<sub>2</sub> based samples, suggesting no obvious change in the TiO<sub>2</sub>.



**Fig. S11** XRD patterns of TiO<sub>2</sub>-Pd-Au-L, TiO<sub>2</sub>-Pd-Au and TiO<sub>2</sub>-Pd-Au-H. The bottom corresponds to the standard XRD patterns for TiO<sub>2</sub> (black, JCPDS No. 21-1272), Pd (red, JCPDS No. 65-2867) and Au (blue, JCPDS No. 65-2870). It can be clearly seen that the intensities of Au peaks gradually increase from TiO<sub>2</sub>-Pd-Au-L to TiO<sub>2</sub>-Pd-Au, and then to TiO<sub>2</sub>-Pd-Au-H, while there is no obvious change in the intensity of Pd peaks, further confirming the gradually increased amount of Au in the samples.



**Fig. S12** (a,b) TEM images of  $TiO_2$ -PdH<sub>0.43</sub>-Au; (c) XRD patterns of  $TiO_2$ -PdH<sub>0.43</sub>-Au and  $TiO_2$ -Pd-Au. The bottom corresponds to the standard XRD patterns for  $TiO_2$  (black, JCPDS No. 21-1272), Pd (red, JCPDS No. 65-2867) and Au (blue, JCPDS No. 65-2870); (d) Average CH<sub>4</sub> production rates of  $TiO_2$ -PdH<sub>0.43</sub>-Au and  $TiO_2$ -Pd-Au under UV light irradiation.

Sample	Molar ratio of TiO <sub>2</sub> : Pd : Au
TiO <sub>2</sub> -Pd	100 : 3.1 : 0
TiO <sub>2</sub> -Au	100 : 0 : 2.5
TiO <sub>2</sub> -Pd-Au	100 : 3.2 : 2.4
TiO <sub>2</sub> -Pd/Au	100 : 3.1 : 2.5
TiO <sub>2</sub> -Pd@Au	100 : 3.0 : 3.7
TiO <sub>2</sub> -Au@Pd	100 : 4.4 : 2.6
TiO <sub>2</sub> -PdAu	100 : 3.2 : 2.3
TiO <sub>2</sub> -Pd-Au-L	100 : 3.1 : 0.7
TiO <sub>2</sub> -Pd-Au-H	100 : 3.2 : 8.2

**Table S1.** Chemical compositions of TiO<sub>2</sub>-Pd, TiO<sub>2</sub>-Au, TiO<sub>2</sub>-Pd-Au, TiO<sub>2</sub>-Pd/Au, TiO<sub>2</sub>-Pd@Au, TiO<sub>2</sub>-Au@Pd and TiO<sub>2</sub>-PdAu samples determined by ICP-MS.

	Metal	Average CH <sub>4</sub>	Selectivity for	
Semiconductor	co-catalyst	production rate	CH <sub>4</sub> production	Ref.
		$(\mu mol g_{cat}^{-1} h^{-1})$	(%)	
TiO <sub>2</sub>	Pd	4.1	35.7	20
TiO <sub>2</sub>	Rh	4.5	15.7	24
TiO <sub>2</sub>	PdCu	19.6	96	28
TiO <sub>2</sub>	Pt	5.2	37.9	43
TiO <sub>2</sub>	Au	3.1	36.6	43
TiO <sub>2</sub>	Pd	4.3	39.7	43
TiO <sub>2</sub>	AuPd	14.3	71	44
TiO <sub>2</sub>	PtRu	38.7	93.7	45
TiO <sub>2</sub>	Pd-Au	48.2	91.4	*

**Table S2.** Comparison of the photocatalytic activity of as-obtained  $TiO_2$ -Pd-Au with those of previously reported metal and bimetal co-catalysts supported by  $TiO_2$ .

\* The photocatalytic activity of TiO<sub>2</sub>-Pd-Au reported by us.

## References

- S1 X. Han, Q. Kuang, M. Jin, Z. Xie and L. Zheng, J. Am. Chem. Soc., 2009, 131, 3152–3153.
- S2 T. Sun, R. Simmons, D. Huo, B. Pang, X. Zhao, C. W. Kim, H. Jo and Y. Xia, *ChemNanoMat*, 2016, 2, 400–406.
- S3 Y. Zhu, Z. Xu, W. Jiang, S. Zhong, L. Zhao and S. Bai, J. Mater. Chem. A, 2017, 5, 2619–2628.