Electronic Supplementary Information (ESI)

Vacancy engineering of AuCu cocatalysts for improving photocatalytic conversion of CO_2 to CH_4

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Additional experimental

Chemical. Copper acetylacetonate ($Cu(acac)_2$, Aladdin, C109323), 1-adamantanecarboxylic acid (ACA, Aladdin, A107246), 1,2-hexadecanediol (HDD, Aladdin, H129154), 1-hexadecylamine (HDA, Aladdin, H105442), 1-dodecanethiol (DDT, Aladdin, D105610), diphenyl ether (DPE, Aladdin, D110644), 3-mercaptopropionic acid (MPA, Aldrich, M5801), cuprous bromide (CuBr, Aladdin, C104698), trioctylphosphine oxide (TOPO, Aladdin, T106624), oleylamine (Aladdin, O106967) were used in the synthesis. All the other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. The water used in all the experiments was deionized. All chemicals were used as received without further purification.

Synthesis of TiO_2 nanosheets. TiO_2 nanosheets were synthesized by modifying a method in literature with hydrofluoric acid as a capping agent.[S1] Caution! Hydrofluoric acid is extremely corrosive and toxic, and should be handled with extreme care.

Synthesis of TiO_2-Au. The TiO_2-Au was synthesized with the deposition of Au nanocubes on TiO_2 nanosheets. In a typical synthesis of Au nanocubes,[S2] an aqueous solution of $HAuCl_4 \cdot 4H_2O$ (0.25 mL, 10 mM) was added into an aqueous solution of cetyltrimethylammounium bromide (CTAB, 7.5 mL, 100 mM), and mixed by magnetic stirring. Then added the freshly prepared $NaBH_4$ solution (0.6 mL ,10 mM) stirred for 2 min. Next, the solution was left undisturbed at 25 °C for 1 h. This solution was diluted 10 times with water and used as a seed solution for the synthesis of Au nanocubes. An aqueous solution of $HAuCl_4 \cdot 4H_2O$ (0.20 mL, 10 mM) was added to a solution containing 8.0 mL H_2O and CTAB solution (1.6 mL, 100 mM). Subsequently, an aqueous ascorbic acid (AA) solution (0.95 mL, 100 mM) was added. Finally, 5 μL of the 1 h aged Au seed solution was added to the reaction mixture, which was then kept undisturbed for 1 h. The product was collected by centrifugation, and washed with water at 8000 rpm for several times and dispersed in water. The deposition of Au nanocubes on TiO_2 nanosheets was achieved by ultrasonic treatment of a mixed suspension of Au nanocubes and TiO_2 nanosheets, followed by a post-treatment. 50 mg of TiO_2 nanosheets were dispersed in 10 mL of an aqueous solution containing 50 μL of $NH_3 \cdot H_2O$ (28%) and 50 μL of MPA by sonication. Then 2 mL aqueous suspension of Au nanocubes (0.01 mmol mL^{-1}) was added under sonication for 10 min. The product was separated by centrifugation, washed with the mixture of water and ethanol three times, dried at 45 °C in a vacuum, and finally annealed at 120 °C for 2 h under Ar atmosphere.

Synthesis of TiO_2-Cu. The TiO_2-Cu was synthesized with the deposition of Cu nanocubes on TiO_2 nanosheets. In a typical synthesis of Cu nanocubes,[S3] under Ar atmosphere, CuBr (0.5 mmol), TOPO (2.0 mmol) and oleylamine (45.0 mmol) were mixed in three-neck round-bottom flask (50 mL). The Ar flow was kept for 15 min at room-temperature to remove the O_2 in the apparatus and heated in 80 °C for 30 min. Then, the reaction was heated and stirred at 230 °C for 3 h. The sample was collected by centrifugation, and washed with n-hexane for three times, and re-dispersed in a mixture of n-hexane and ethanol (volume ratio of 5 : 1). The deposition of Cu nanocubes on TiO_2 nanosheets was achieved by ultrasonic treatment of a mixed suspension of Cu nanocubes and TiO_2 nanosheets, followed by a post-treatment. 50 mg of TiO_2 nanosheets were dispersed by sonication in a mixture of n-hexane and ethanol (volume ratio of 5 : 1). Subsequently, 2 mL of Cu nanocubes suspension (0.01 mmol mL^{-1}) in a mixture of n-hexane and ethanol (volume ratio of 5 : 1) was added under sonicated for 10 min. The product was separated by centrifugation, washed with the mixture of water and ethanol three times, dried at 45 °C in a vacuum, and finally annealed at 120 °C for 2 h under Ar atmosphere.

Sample characterizations. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images, selected-area electron diffraction (SAED) pattern, scanning TEM (STEM) images and energy dispersive 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 X-ray diffractometer with Non-monochromated Cu-Kα X-Ray. X-ray photoelectron spectra (XPS) were collected on an ESCALab 250 X-ray photoelectron spectrometer, using nonmonochromatized Al-Kα X-ray as the excitation source. UV-vis 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 examined using a HITACHI F-7000

Spectrofluorometer. Energy dispersive X-ray (EDX) spectrum was performed with a Hitachi S-4800 scanning electron micro-analyzer with an accelerating voltage of 15 kV.

Photoelectrochemical measurements. 3.0 mg of as-synthesized products were dispersed in a mixture of 10 μL ethanol and 10 μL Nafion, which were then uniformly spin-dropped onto at a 1 cm × 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 (PLS-SXE300/300UV, Beijing Perfectlight, China). Both visible and broad-spectrum light were used as the illumination source. Visible light was realized using both a 400-nm cutoff filter (long-wave-pass) and a 780-nm cutoff filter (short-wave-pass), while broad-spectrum light was realized in the presence of a 780-nm cutoff filter (short-wave-pass). UV light was used as the illumination source, which was realized in the presence of a short-wave-pass 400 nm cutoff filter. The power density of UV light was measured to be 2.7 mW cm^{-2}. 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_2SO_4 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 600 s. Electrochemical impedance spectroscopy (EIS) was performed in the 10^{-1} to 10^{5} Hz frequency range with an AC voltage amplitude of 10 mV at an applied potential of 0.4 V *vs.* Ag/AgCl.

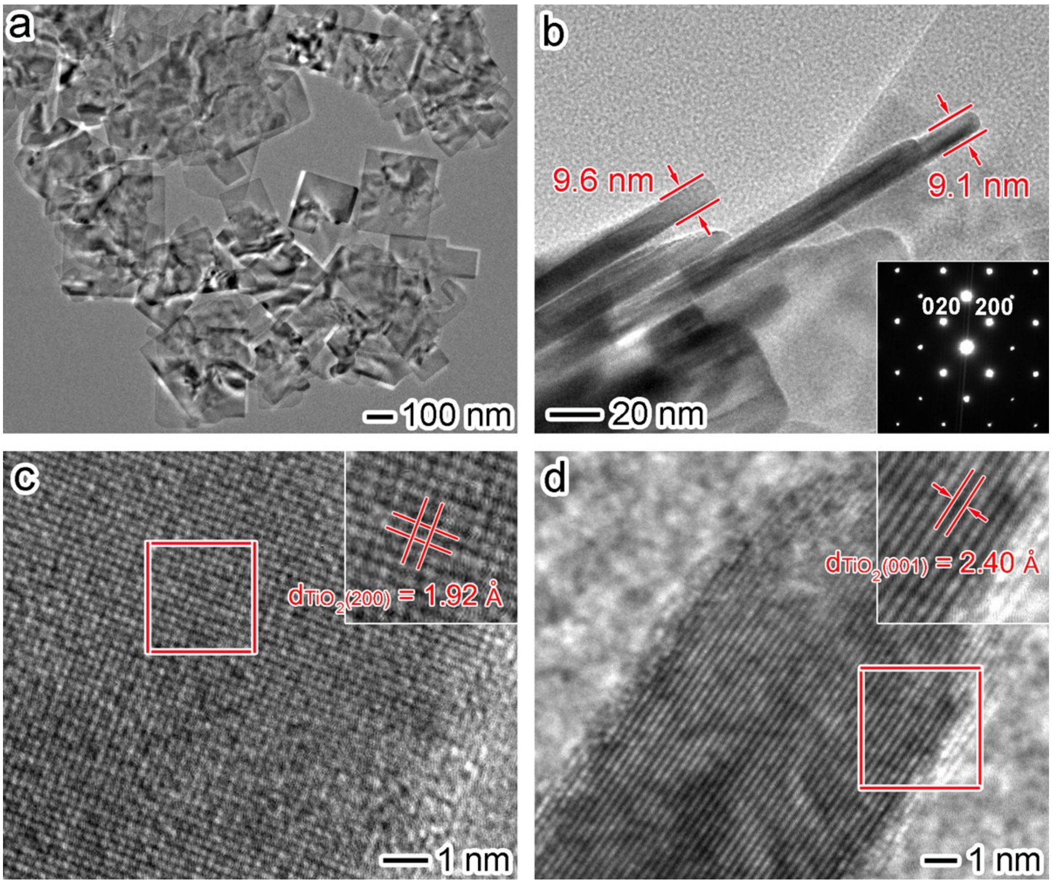

Fig. S1 (a,b) TEM and (c,d) HRTEM images of TiO_2 nanosheets: (a) TEM image showing the flat surface of nanosheets; (b) TEM image showing the cross section and thickness of a nanosheet; (c) HRTEM image taken from a flat face of nanosheet; (d) HRTEM image taken from a cross section of nanosheet; inset of (b) shows the SAED pattern of the nanosheet.

The continuous crystalline lattice with the same crystallographic orientations in the HRTEM images as well as the selected-area electron diffraction (SAED) pattern confirms the monocrystalline structure of TiO_2 nanosheets.[S1]

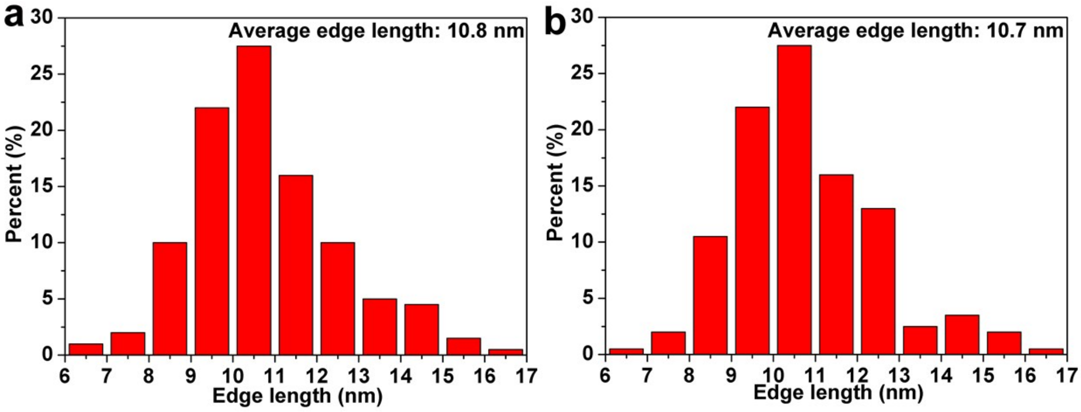

Fig. S2 Size distribution histograms and average edge lengths of AuCu nanocubes on TiO_2 nanosheets: (a) before acid treatment and (b) after acid treatment.

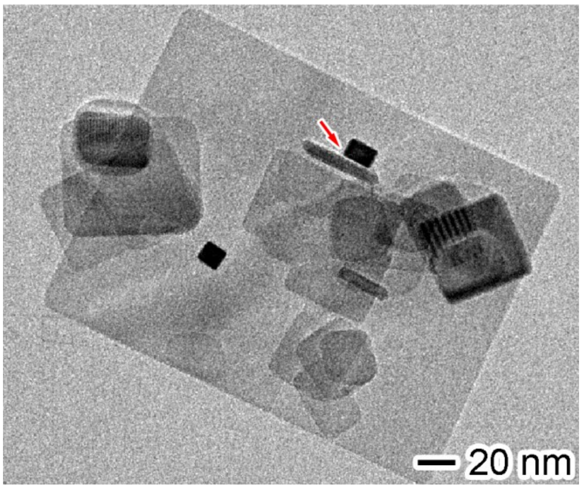

Fig. S3 TEM image of TiO_2-AuCu with a standing-up TiO_2 nanosheet.

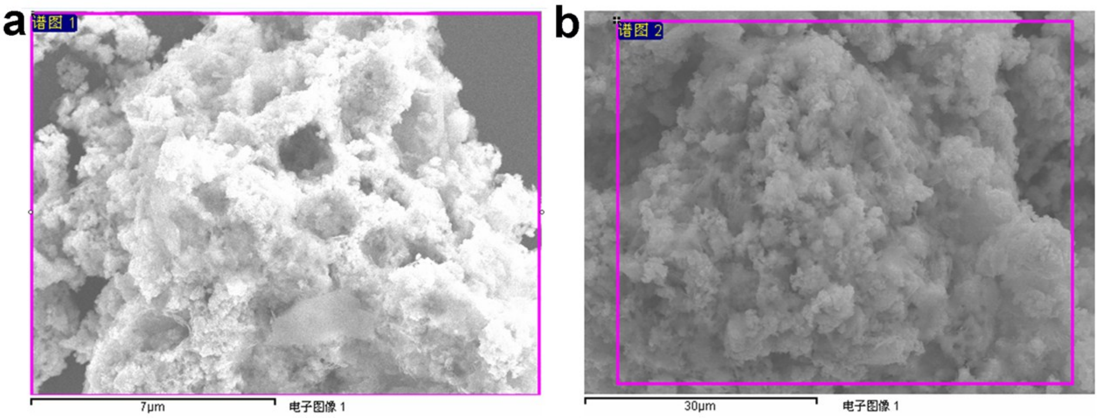

Fig. S4 SEM images of (a) TiO_2-AuCu and (b) TiO_2-AuCu-V corresponding to EDX spectra in Fig. 2a and b, respectively.

It can be seen that the EDX spectra was measured from a large selected area in the SEM images, guaranteeing the accuracy of the test.

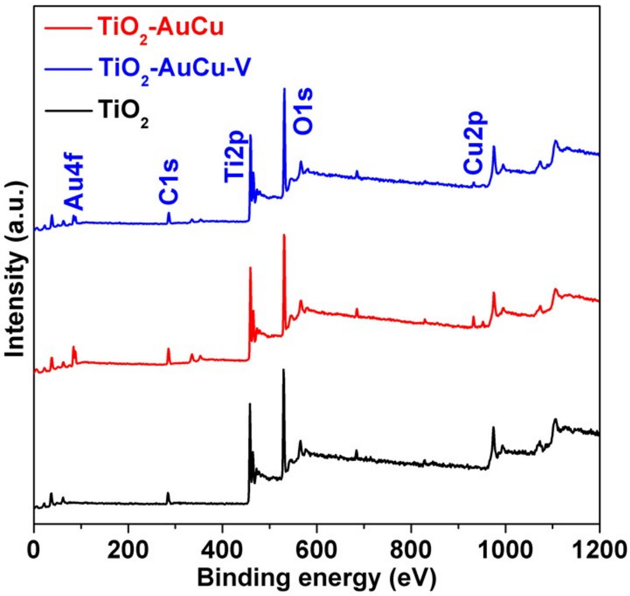

Fig. S5 Survey spectra of TiO_2, TiO_2-AuCu and TiO_2-AuCu-V.

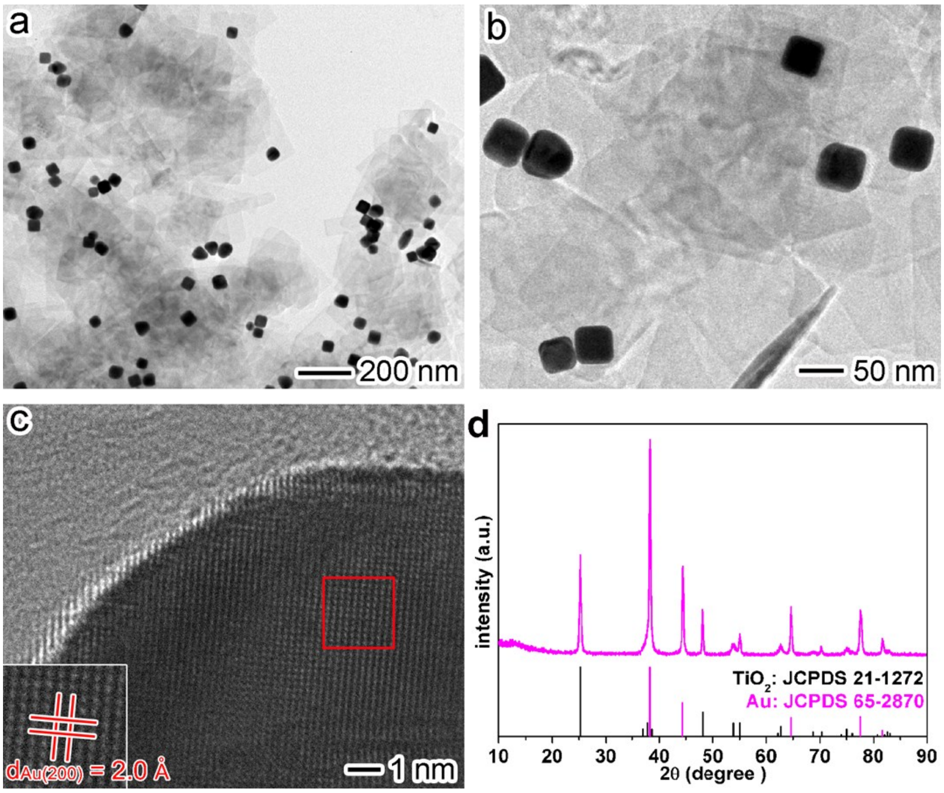

Fig. S6 (a,b) TEM images, (c) HRTEM image and (d) XRD pattern of TiO_2-Au.

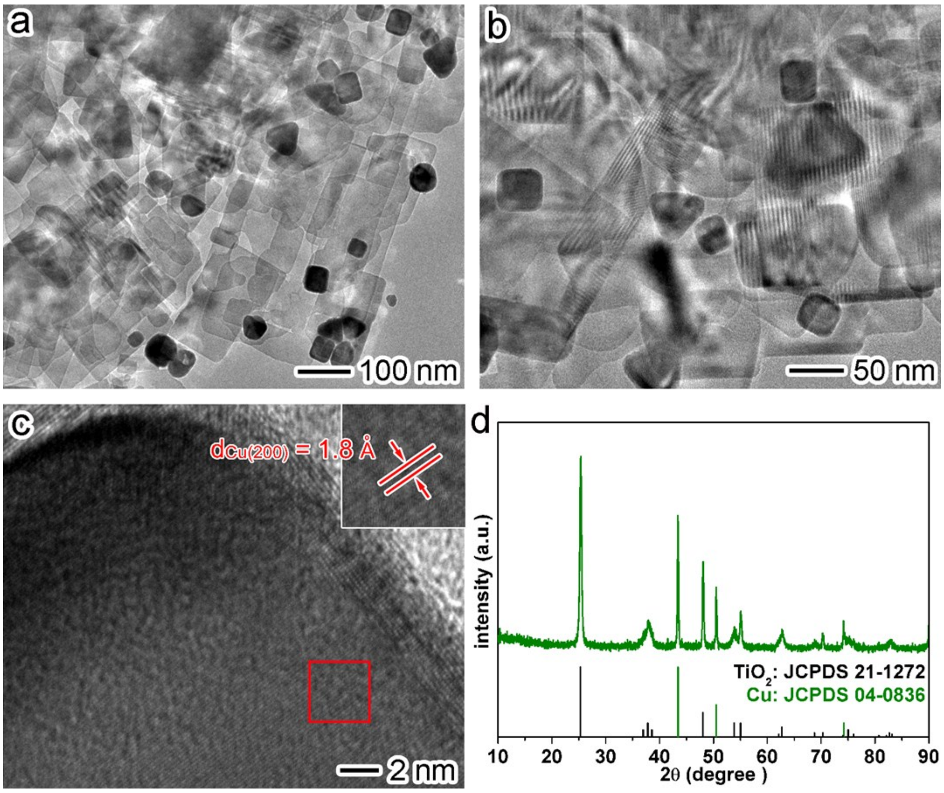

Fig. S7 (a,b) TEM images, (c) HRTEM image and (d) XRD pattern of TiO_2-Cu.

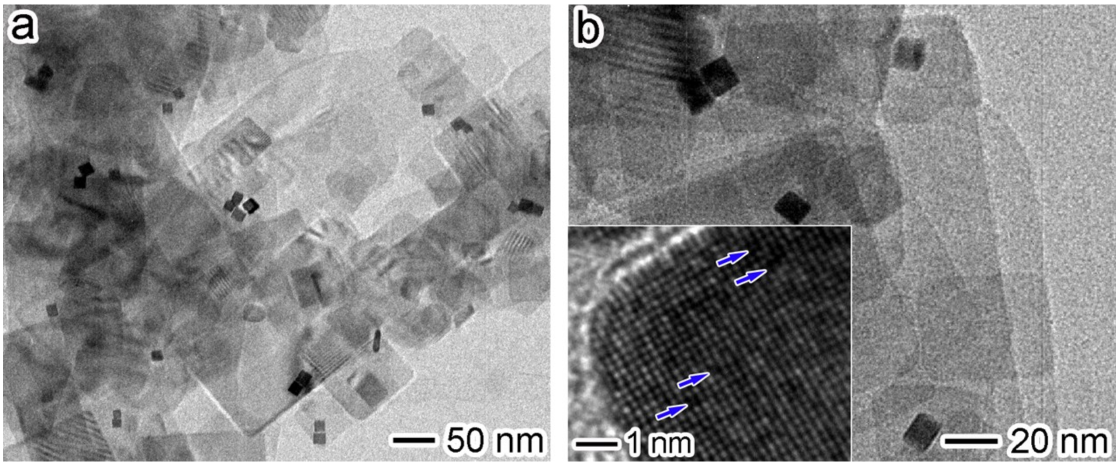

Fig. S8 TEM and HRTEM (inset of b) images of TiO_2-AuCu-V after the photocatalytic cyclic process.

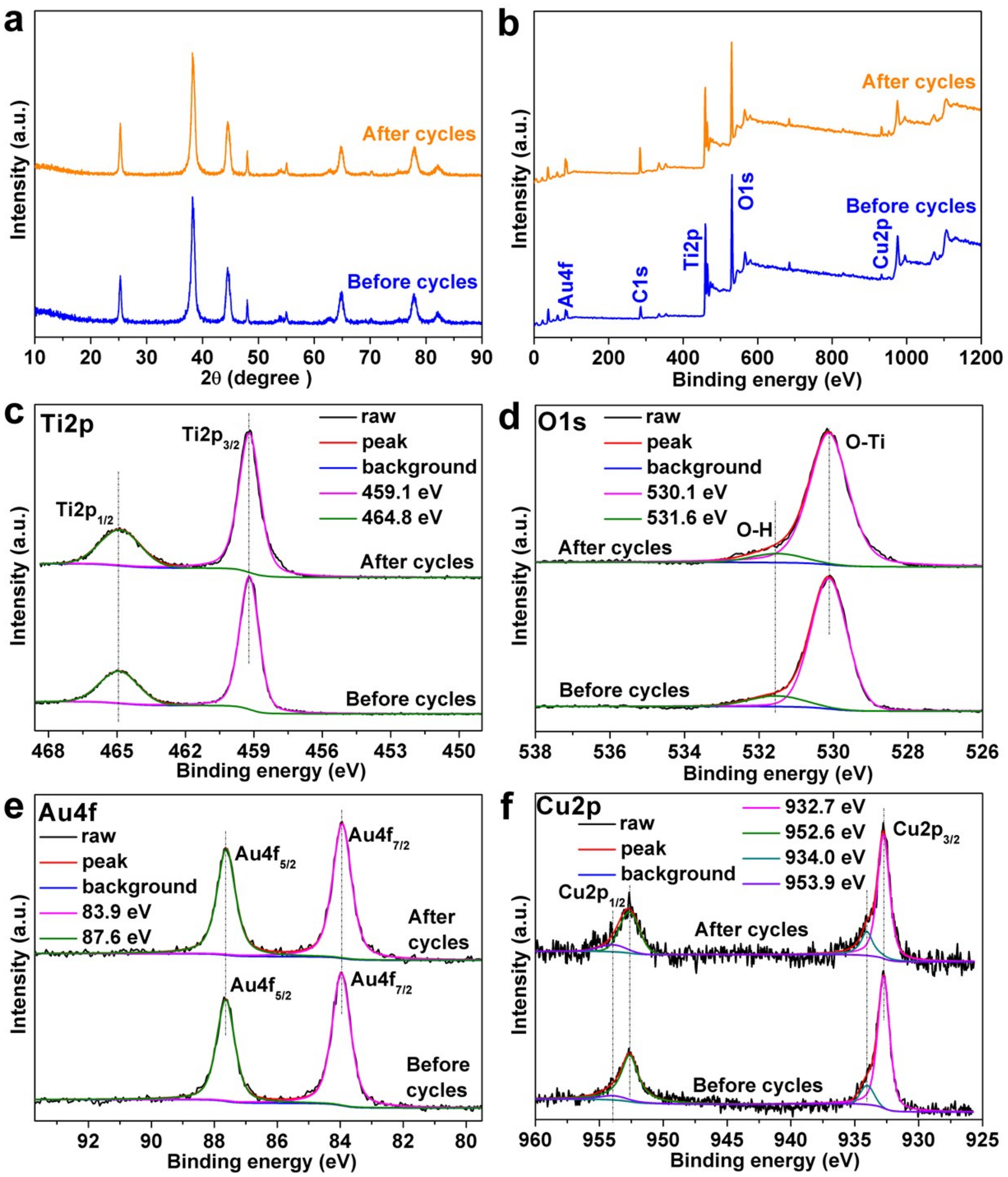

Fig. S9 (a) XRD patterns and (b-f) XPS spectra of TiO_2-AuCu-V before and after the photocatalytic cyclic process: (b) survey spectra, (c) Ti2p, (d) O1s, (e) Au4f and (f) Cu2p high-resolution spectra.

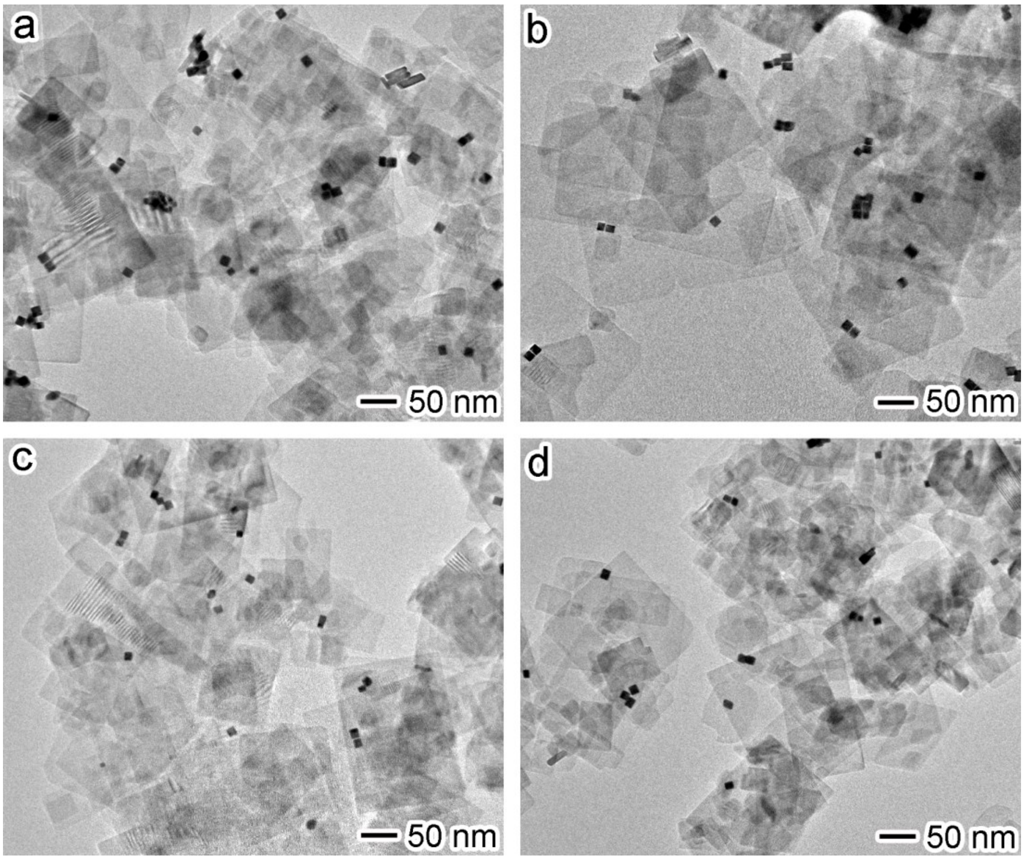

Fig. S10 TEM images of TiO_2-AuCu-V treated with acetic acid for (a) 1, (b) 3, (c) 7 and (d) 10 h.

Table S1 Comparison of the photocatalytic performance of as-obtained TiO_2-AuCu-V with those of previously reported metal cocatalysts supported by TiO_2.

Semiconductor	Metal cocatalyst	Average CH_4 production rate (μmol g_{cat}^{-1} h^{-1})	Selectivity for CH_4 production (%)	Ref.
TiO_2	Pd	4.1	35.7	28
TiO_2	Rh	4.5	15.7	29
TiO_2	Pt	5.2	37.9	
TiO_2	Au	3.1	36.6	44
TiO_2	Pd	4.3	39.7	
TiO_2	AuPd	14.3	71.0	45
TiO_2	PtCu	11.3	—	46
TiO_2	AuCu	33.5	94.7	★

★ The photocatalytic activity of TiO_2-AuCu-V reported by us.

References

S1 X. Han, Q. Kuang, M. Jin, Z. Xie and L. Zheng, *J. Am. Chem. Soc.*, 2009, **131**, 3152.

S2 M. Laskar, X. Zhao, Z. Y. Li and S. E. Skrabalak, *ChemSusChem*, 2013, **6**, 1959.

S3 N. Suen, Z. Kong, C. Hsu, H. Chen, C. Tung, Y. Lu, C. Dong, C. Shen, J. Chung and H. Chen, *ACS Catal.*, 2019, **6**, 5217.