Electronic Supplementary Information (ESI)

Ordered engineering on the lattice of intermetallic PdCu co-catalysts in boosting the photocatalytic conversion of CO₂ into CH₄

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Additional experimental

Chemicals. Palladium (II) acetylacetonate (Pd(acac)₂, Aladdin, P101065), copper (II) acetylacetonate (Cu(acac)₂, Aladdin, C109323) and oleylamine (Aladdin, O106967) were used in our synthesis. All other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. without further purification. The water used in all experiments was de-ionized.

Synthesis of C₃N₄ **nanosheets.** Bulk g-C₃N₄ was synthesized through a modified method according to previous reports.^{S1} In a typical synthesis, 20 g of urea was dissolved in 10 mL water. The obtained solution was heated at 550 °C for 3 h (0.5 °C/min ramp rate; natural cooling). Then the resultant yellow agglomerates were milled into g-C₃N₄ powder in a mortar. The as-synthesized g-C₃N₄ powder was further dispersed in cyclohexane/ethanol mixture to form the corresponding suspension of C₃N₄ nanosheets with probe sonication for 1 h, respectively.

Synthesis of TiO₂ nanosheets. The TiO₂ nanosheets were synthesized by modifying a method in literature with hydrofluoric acid as a capping agent.^{S2} In a typical synthesis, 10-mL of tetrabutyl titanate was added into a 50-mL dried Teflon autoclave. Then with vigorous magnetic stirring, 2.5 mL of hydrofluoric acid was added and the stirring was allowed to proceed for 5 min. Then the Teflon-lined stainless steel autoclave was heated at 200 °C for 24 h. After the autoclave had cooled down to room temperature, the resultant product was separated by centrifugation, and washed with water for several times. The final product was then dried at 45 °C for 12 h. Caution! Hydrofluoric acid is extremely corrosive and toxic, and should be handled with extreme care.

Synthesis of TiO₂ based samples. TiO_2 -Pd₁Cu₂ was synthesized by following the same procedure for C_3N_4 -Pd₁Cu₂ except the use of 100 mg of TiO₂ nanosheets instead of 20 mg of C₃N₄. The TiO₂-Pd₁Cu₂ was converted to corresponding TiO₂-Pd₁Cu₂-250 and TiO₂-Pd₁Cu₂-375 samples according to the same annealing

treatment in the synthesis of C_3N_4 -Pd₁Cu₂-250 and C_3N_4 -Pd₁Cu₂-375 samples, respectively.

Sample characterizations. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) images, 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-Ka X-Ray. Fourier Transform infrared spectra (FTIR) were performed with a NEXUS 670 Spectrometer. 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. The concentrations of Pd and Cu elements were measured as follows: the samples were dissolved with a mixture of HNO₃ and HCl (1 : 3, volume ratio), which was then diluted with 1% HNO₃. The concentrations of metal ions were then measured through a Thermo Scientific PlasmaQuad 3 inductively-coupled plasma mass spectrometry (ICP-MS). The loading amounts of PdCu on the C₃N₄ nanosheets were determined by sample weighing prior to the dissolution of PdCu for the ICP-MS measurements.



Fig. S1 (a) SEM image of bulk C_3N_4 ; (b) TEM image of C_3N_4 nanosheets.



Fig. S2 Size distribution histograms of PdCu nanocrystals on the C_3N_4 nanosheets: (a) C_3N_4 -Pd₁Cu₂, (b) C_3N_4 -Pd₁Cu₂-250 and (c) C_3N_4 -Pd₁Cu₂-375.



Fig. S3 (a) Survey XPS spectra of pristine C_3N_4 , C_3N_4 -Pd₁Cu₂, C_3N_4 -Pd₁Cu₂-250 and C_3N_4 -Pd₁Cu₂-375; (b) valence-band XPS spectra of pristine C_3N_4 , C_3N_4 -Pd₁Cu₂, C_3N_4 -Pd₁Cu₂-250 and C_3N_4 -Pd₁Cu₂-375; (c) C1s and (d) N1s high-resolution spectra of pristine C_3N_4 .



Fig. S4 Cu LMM Auger spectra of C_3N_4 -Pd₁Cu₂, C_3N_4 -Pd₁Cu₂-250 and C_3N_4 -Pd₁Cu₂-375.



Fig. S5 (a) UV-vis-NIR absorption spectra of ethanol suspensions containing pure Pd_1Cu_2 nanoparticles (inset is the photograph of ethanol suspensions containing Pd_1Cu_2 nanoparticles); (b) photograph of (I) C_3N_4 , (II) C_3N_4 -Pd_1Cu_2, (III) C_3N_4 -Pd_1Cu_2-250 and (IV) C_3N_4 -Pd_1Cu_2-375 powders.



Fig. S6 Size distribution histograms of PdCu nanocrystals on the C_3N_4 nanosheets: (a) C_3N_4 -Pd₁Cu₁; (b) C_3N_4 -Pd₂Cu₁; (c) C_3N_4 -Pd₁Cu₁-375 and (d) C_3N_4 -Pd₂Cu₁-375.



Fig. S7 XRD patterns of C_3N_4 -Pd₁Cu₁ and C_3N_4 -Pd₂Cu₁.



Fig. S8 (a) Survey XPS spectra, (b) valence-band XPS spectra and (c) Cu LMM Auger spectra of C_3N_4 -Pd₁Cu₂-375, C_3N_4 -Pd₁Cu₁-375 and C_3N_4 -Pd₂Cu₁-375.



Fig. S9 (a) UV-vis-NIR absorption spectra of ethanol suspensions containing pure Pd_1Cu_2 , Pd_1Cu_1 and Pd_2Cu_1 nanoparticles (inset is the photograph of ethanol suspensions containing Pd_1Cu_2 , Pd_1Cu_1 and Pd_2Cu_1 nanoparticles); (b) photograph of (I) C_3N_4 - Pd_1Cu_2 , (II) C_3N_4 - Pd_1Cu_1 , (III) C_3N_4 - Pd_2Cu_1 , (IV) C_3N_4 - Pd_1Cu_2 -375, (V) C_3N_4 - Pd_1Cu_1 -375 and (VI) C_3N_4 - Pd_2Cu_1 -375 powders.



Fig. S10 TEM images of C_3N_4 -Pd₁Cu₂-375 after the photocatalytic cycles.



Fig. S11 (a) XRD patterns and (b-f) XPS spectra of C_3N_4 -Pd₁Cu₂-375 before and after the photocatalytic cycles: (b) survey spectra, (c) C1s, (d) N1s, (e) Pd3d and (f) Cu2p high-resolution spectra.



Fig. S12 TEM images of (a,b) TiO₂, (c,d) TiO₂-Pd₁Cu₂, (e,f) TiO₂-Pd₁Cu₂-250 and (g,h) TiO₂-Pd₁Cu₂-375.



Fig. S13 (a-c) TEM and HRTEM images of C_3N_4 -Pd₁Cu₂-500; (d) size distribution histograms of PdCu nanocrystals in C_3N_4 -Pd₁Cu₂-500; (e) XRD pattern of C_3N_4 -Pd₁Cu₂-500; (f) average H₂, CO, and CH₄ evolution rates with C_3N_4 -Pd₁Cu₂-500 as photocatalyst as well as its selectivity in CH₄ production under visible light (420 < λ < 780 nm) irradiation.

The C_3N_4 -Pd₁Cu₂ was also annealed at 500 °C under a 5% H₂/95% N₂ atmosphere for 1 h to obtain C_3N_4 -Pd₁Cu₂-500 sample. As shown in Fig. S13a and b, there is no obvious change in the morphology of Pd₁Cu₂ nanocrystals on C_3N_4 nanosheets, while

the average size increases to 7.1 nm (Fig. S13d). Moreover, from the HRTEM image (Fig. S13c) and XRD pattern of the C_3N_4 -Pd₁Cu₂-500 (Fig. S13e), it can be seen that the peaks of A1 phase still exist in addition to those of B2 phase. The possible explain is that the further increasing the annealing temperature leads to sintering of the Pd₁Cu₂ nanocrystals, which prevents the complete conversion of A1 phase to B2 phase.^{S3} As a result, the photocatalytic activity and selectivity of C_3N_4 -Pd₁Cu₂-500 in CH₄ production decrease in comparison with those of C_3N_4 -Pd₁Cu₂-375 (Fig. S13f).



Fig. S14 (a-f) TEM and HRTEM images of (a-c) C_3N_4 -Pd₁Cu₃ and (d-f) C_3N_4 -Pd₁Cu₃-375; (g) XRD patterns of C_3N_4 -Pd₁Cu₃ and C_3N_4 -Pd₁Cu₃-375; (h) schematic illustrating the reduced number of isolated Cu sites and decreased electron trapping ability of Pd₁Cu₃ co-catalysts in C_3N_4 -Pd₁Cu₃ and C_3N_4 -Pd₁Cu₃-375; (i) average H₂, CO, and CH₄ evolution rates with C_3N_4 -Pd₁Cu₃ and C_3N_4 -Pd₁Cu₃-375 as photocatalyst as well as their selectivities in CH₄ production under visible light (420 $< \lambda < 780$ nm) irradiation.

The C₃N₄-Pd₁Cu₃ sample with the molar ratio of Pd(acac)₂ to Cu(acac)₂ of 1 : 3 was also synthesized with 5.7 mg of Pd(acac)₂ and 14.7 mg of Cu(acac)₂, which was further annealed at 375 °C under a 5% H₂/95% N₂ atmosphere for 1 h to obtain C₃N₄-Pd₁Cu₃-375 sample. The TEM images of as-synthesized C₃N₄-Pd₁Cu₃ and C₃N₄-Pd₁Cu₃-375 suggest that the molar ratios of Pd/Cu can be further decreased to obtain the nanosheet-supported nanoparticle structures (Fig. S14a,b and d,e). Moreover, the comparison of the HRTEM images (Fig. S14c and f) and XRD patterns (Fig. S14g) of the two samples indicates that the A1 phase of Pd_1Cu_3 nanocrystals can not be successfully converted to B2 phase, revealing that the further decreasing the Pd/Cu molar ratio disfavors the formation of ordered B2 phase considering the determined Pd/Cu molar ratio of the B2 phase. As shown in Fig. S14h, the higher Cu content not only reduces the number of isolated Cu sites in the Cu rich Pd_1Cu_3 nanocrystals before and after the annealing treatment, but also decreases their electron trapping abilities. As a result, the photocatalytic activities and selectivities of C_3N_4 - Pd_1Cu_3 and C_3N_4 - Pd_1Cu_3 -375 samples in CH4 production are lower than those of C_3N_4 - Pd_1Cu_2 and C_3N_4 - Pd_1Cu_2 -375 samples, respectively (Fig. S14i).

Table S1 Chemical compositions of C_3N_4 -Pd₁Cu₂, C_3N_4 -Pd₁Cu₂-250, C_3N_4 -Pd₁Cu₂-375, C_3N_4 -Pd₁Cu₁, C_3N_4 -Pd₂Cu₁, C_3N_4 -Pd₁Cu₁-375 and C_3N_4 -Pd₂Cu₁-375 samples determined by ICP-MS.

Sample	Molar ratios of Pd : Cu	Loading amounts of PdCu (wt.%)
C_3N_4 - Pd_1Cu_2	46.9 : 53.1	1.72
$C_{3}N_{4}$ - $Pd_{1}Cu_{2}$ -250	47.3 : 52.7	1.70
$C_{3}N_{4}$ -Pd ₁ Cu ₂ -375	48.4 : 51.6	1.69
C_3N_4 - Pd_1Cu_1	66.6 : 33.4	2.12
C_3N_4 - Pd_2Cu_1	78.7 : 21.3	2.41
$C_{3}N_{4}$ -Pd ₁ Cu ₁ -375	65.2 : 34.8	2.05
$C_{3}N_{4}$ - $Pd_{2}Cu_{1}$ -375	79.2 : 20.8	2.31

Semiconductor	Metal co-catalyst	Average CH ₄ production rate $(\mu mol g_{cat}^{-1} h^{-1})$	Selectivity for CH ₄ production (%)	Ref.
C_3N_4	fcc Pt	0.3	57.1	16
C_3N_4	fcc Pd	0.3	2.5	17
C_3N_4	hcp Ru	0.8	28.4	21
C_3N_4	fcc Pd	0.5	18.2	25
C_3N_4	fcc Pd	0.1	3.4	50
C_3N_4	Ordered bcc	5.0	96.5	*
	Pd_1Cu_2			

Table S2 Comparison of the photocatalytic activity of as-obtained C_3N_4 -Pd₁Cu₂-375 with those of previously reported C_3N_4 supported metal photocatalysts.

* The photocatalytic activity of C_3N_4 -Pd₁Cu₂-375 reported by us.

Reference

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