Supporting Information

Synergistic integration of PdCu alloy on TiO_2 for efficient photocatalytic CO_2 reduction to CH_4 with H_2O

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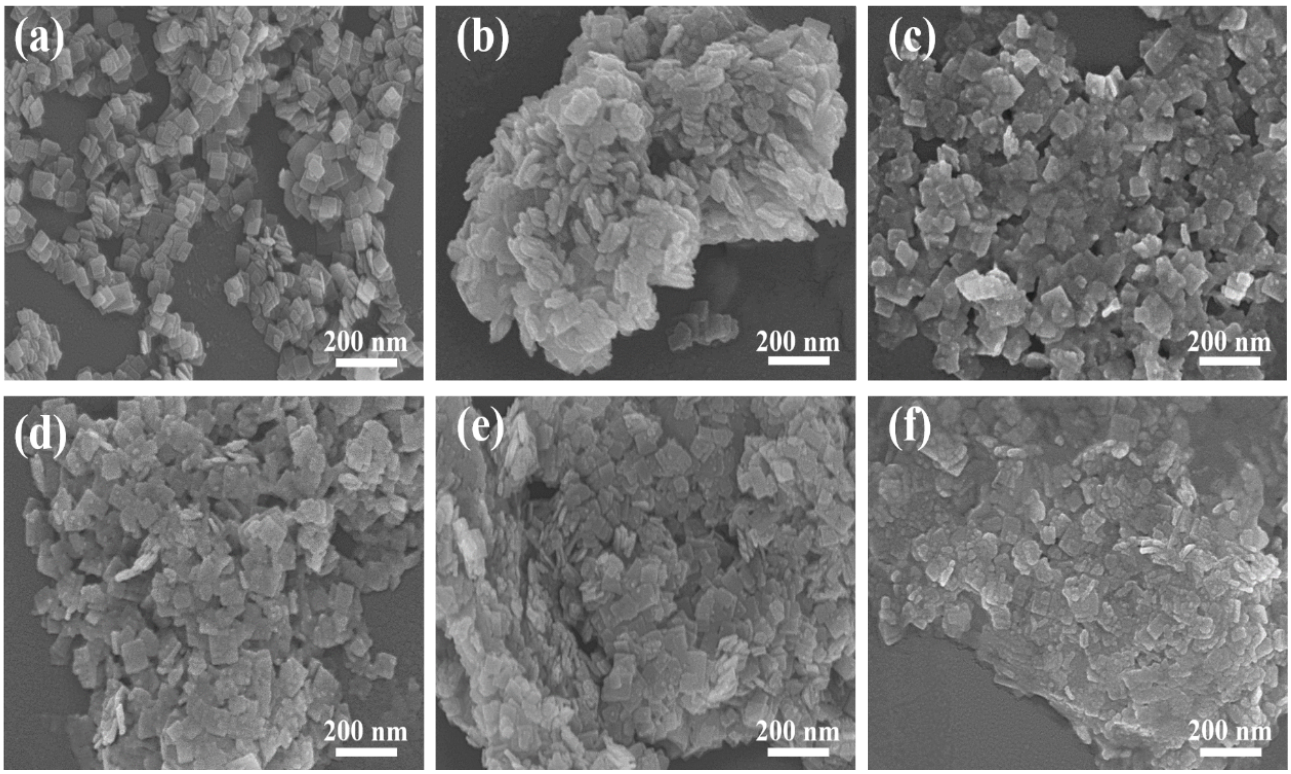

Figure S1. SEM image of the sample (a) TiO_2 NS; (b) Cu-TiO_2 NS; (c) Pd-TiO_2 NS; (d) $(PdCu)_1$-TiO_2 NS; (e) $(PdCu)_2$-TiO_2 NS; (f) $(PdCu)_3$-TiO_2 NS.

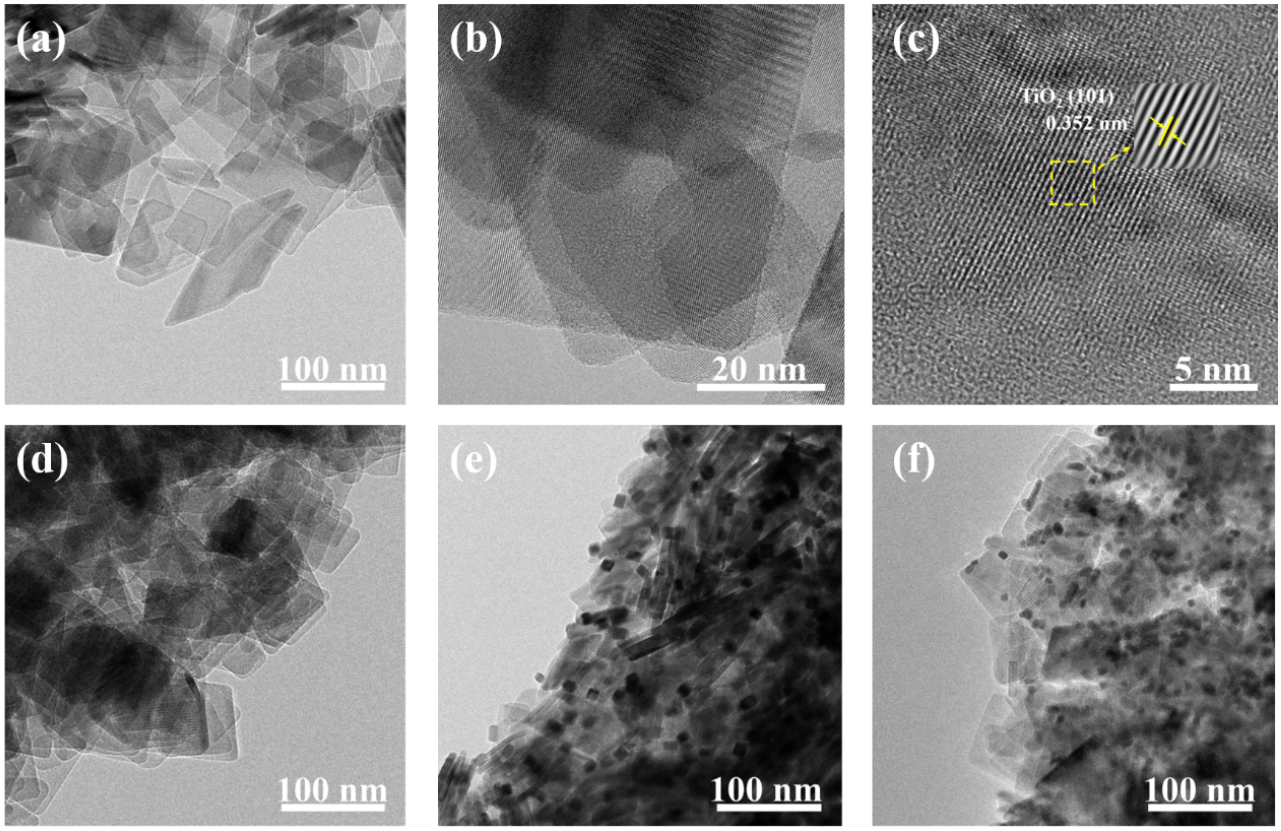

Figure S2. (a, b) Low magnification TEM images of TiO_2 NS; (c) HR-TEM images of TiO_2 NS; low magnification TEM images of some composites (d) Cu-TiO_2 NS; (e) Pd-TiO_2 NS; (f) $(PdCu)_2$-TiO_2 NS.

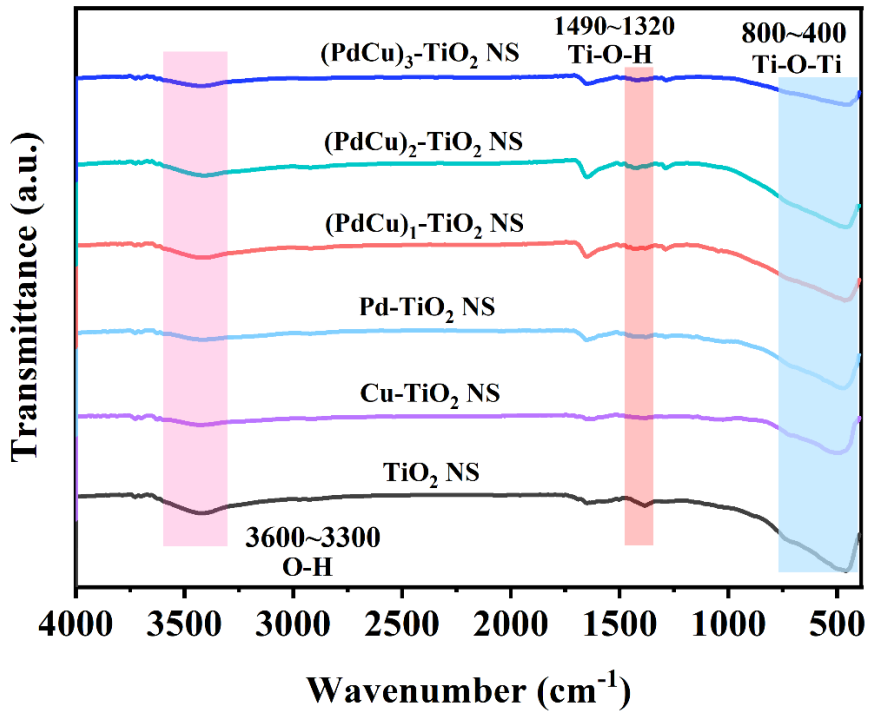

Figure S3. FTIR spectra of TiO_2 NS and its composite materials.

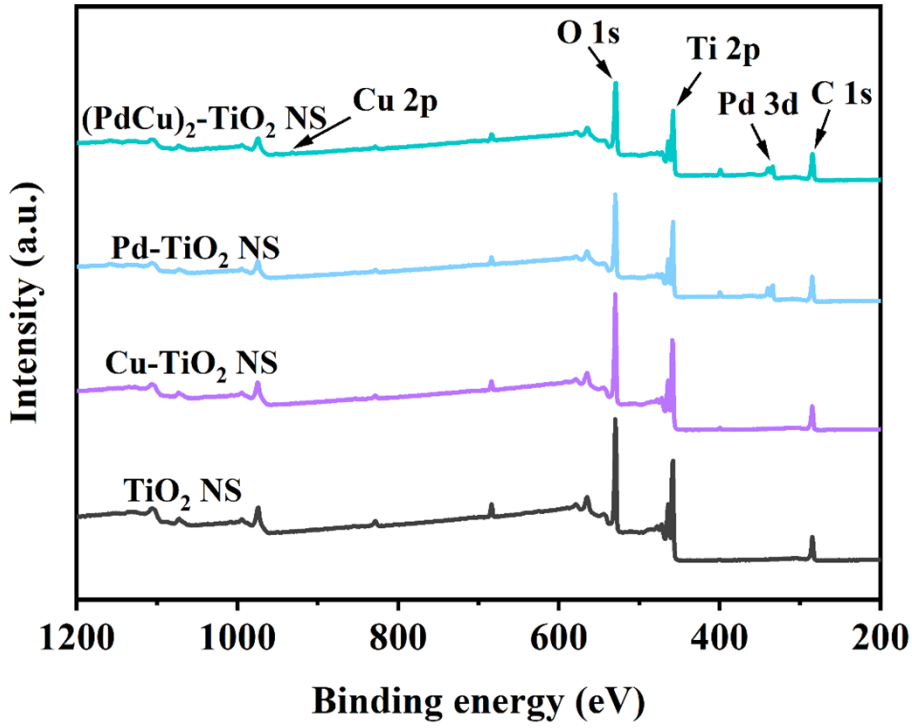

Figure S4. XPS full spectrum of the sample.

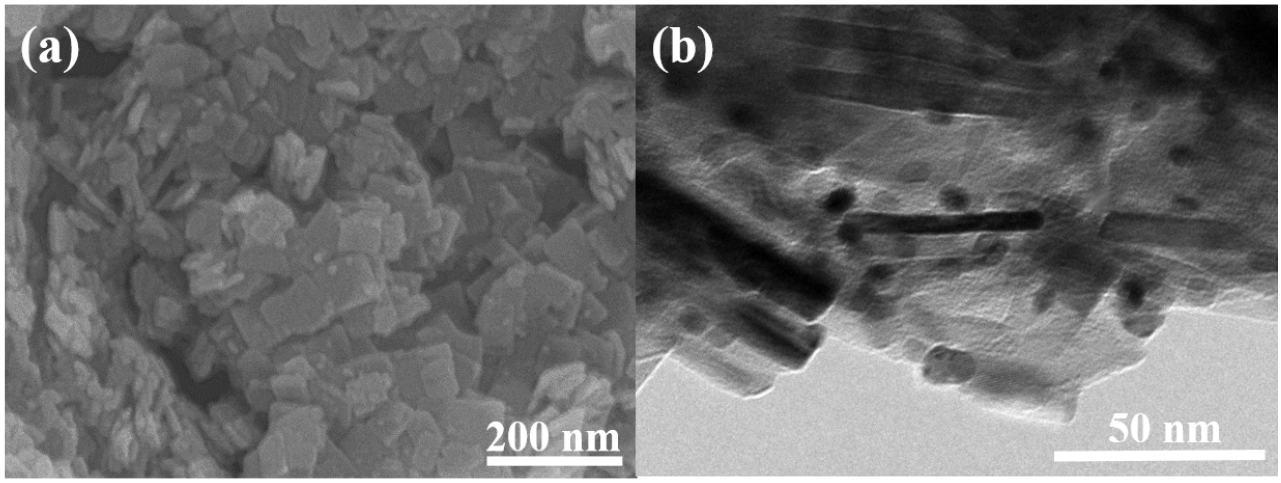

Figure S5. (a) SEM and (b) TEM images of the catalyst after cyclic testing.

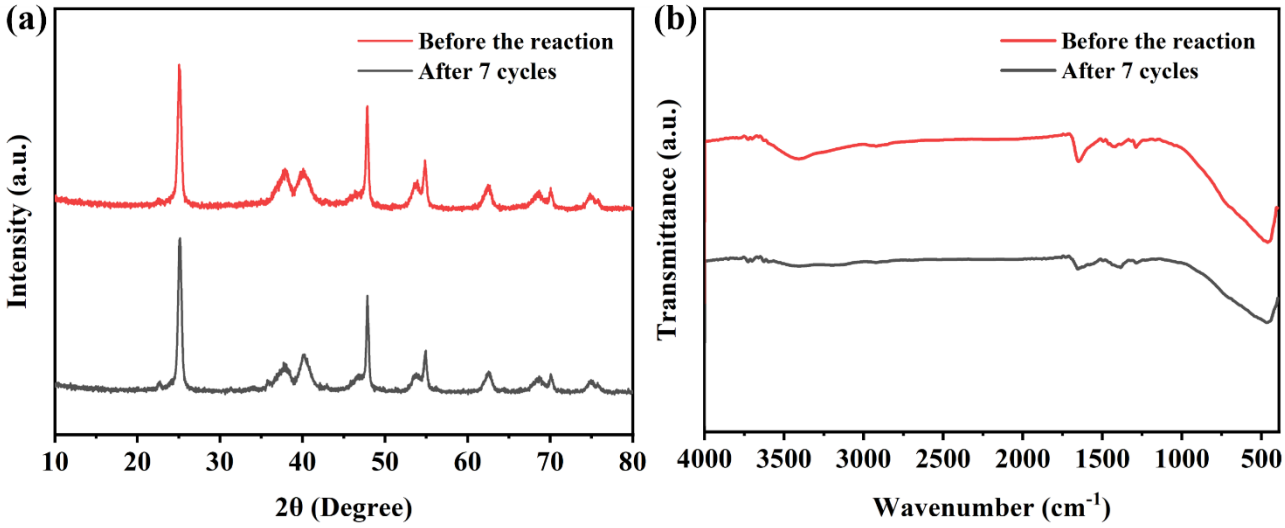

Figure S6. (a) XRD and (b) FT-IR spectra before and after catalyst reaction.

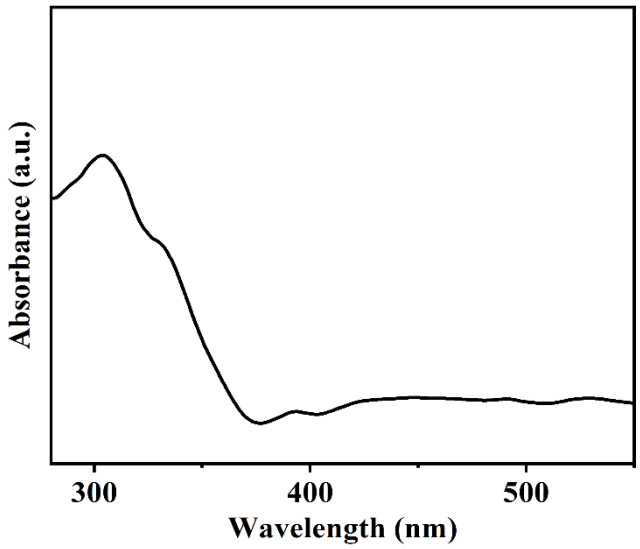

Figure S7. UV-vis spectra after 7 catalyst reactions.

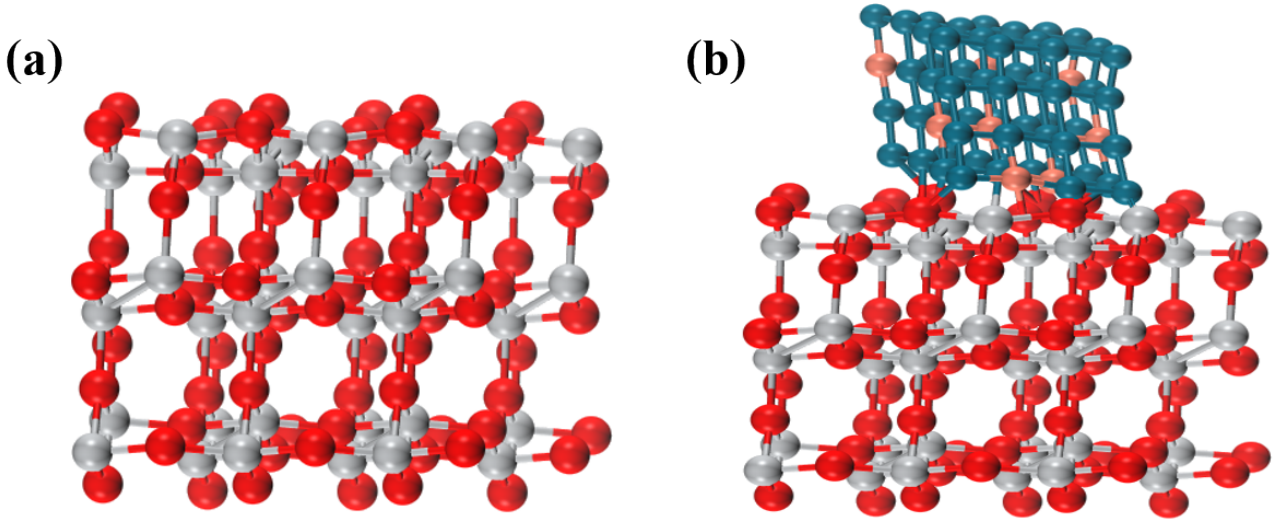

Figure S8. Structural models of optimized (a) TiO_2 and (b) PdCu-TiO_2.

The optimized model of TiO_2 has 108 atoms, 36 Ti, 72 O, which is in accordance with the stoichiometric ratio. The optimized model for PdCu-TiO_2 has 172 atoms, 36 Ti, 72 O, 56 Pd and 8 Cu, which is also in accordance with the stoichiometric ratio.

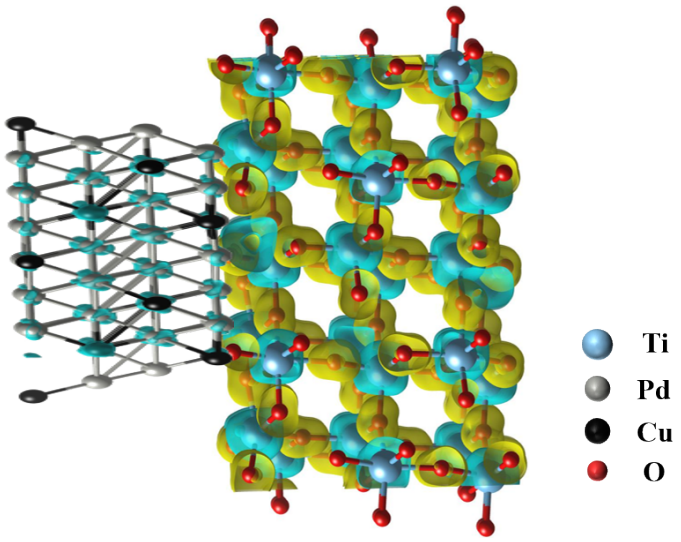

Figure S9. Charge density difference in PdCu-TiO_2 NS.

Table S1. Amount of reagents for the preparation of different samples.

	TiO_2 NS/mg	PVP/mg	AA/mg	KBr/mg	$PdCl_2$/ml	$CuCl_2 \cdot 2H_2O$/ml
$(PdCu)_1$-TiO_2 NS		343.64	60	150	1.55	0.43
$(PdCu)_2$-TiO_2 NS		687.27	120	300	3.1	0.85
$(PdCu)_3$-TiO_2 NS	100	1030.92	180	450	4.65	1.28
Pd-TiO_2 NS		687.27	120	300	3.55	-
Cu-TiO_2 NS		687.27	120	300	-	6.82

Table S2. The mass fraction of metal atoms in the catalyst and the molar ratio between PdCu were determined by ICP-MS.

Photocatalyst	Total mass share of Pd and Cu (%)	Molar ratio of Pd:Cu
Pd-TiO_2	19.2	/
$(PdCu)_1$-TiO_2	9.1	6.83
$(PdCu)_2$-TiO_2	17.9	6.91
$(PdCu)_3$-TiO_2	27.2	6.86
Cu-TiO_2	0.05	/

Table S3. Comparison of the performance of recent research photocatalysts.

Photocatalysts	Light sources	Reaction medium	products	production yield ($\mu mol \cdot g^{-1} \cdot h^{-1}$)	Selectivity	Note	Ref
$(PdCu)_2$-TiO_2 NS	300 W Xe lamp	H_2O vapor	CH_4	18.1	98.7%	/	This work
$Pt_{0.5}Cu_{0.5}/TiO_2$	300 W Xe lamp	H_2O vapor	CH_4	13.5	~97%	Cumbersome process, long preparation cycle	[1]
Cu/TiO_2	300 W Xe lamp	H_2O vapor	CO	15.3	95.9%	Low CH_4 selectivity	[2]
Au-TiO_2	300 W Xe lamp (λ < 420 nm)	H_2O vapor	CO	25.9	83%	High cost, low CH_4 selectivity	[3]
Ag–TiO_2/TS-1	300 W Xe lamp	H_2O vapor	CO	6.8	85%	Low CH_4 selectivity and yield	[4]
Au@ZnS/3DOMm-TiO_2-2	300 W Xe lamp	H_2O vapor	CH_4	33.2	91.5%	High cost, cumbersome process	[5]
BT/ZIS	150 W Xe lamp (AM 1.5G filter)	H_2O+TEOA	CO	71.6	87%	Add sacrificial agent, low CH_4 selectivity	[6]
Pt_1@CN	300 W Xe lamp (AM 1.5G filter)	H_2O vapor	CO	84.8	~100%	Low CH_4 selectivity	[7]

Reference

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