

Electronic Supplementary Information (ESI)

Light-intensity dependence of visible-light CO₂ reduction over Ru(II)-complex/Ag/polymeric carbon nitride hybrid photocatalysts

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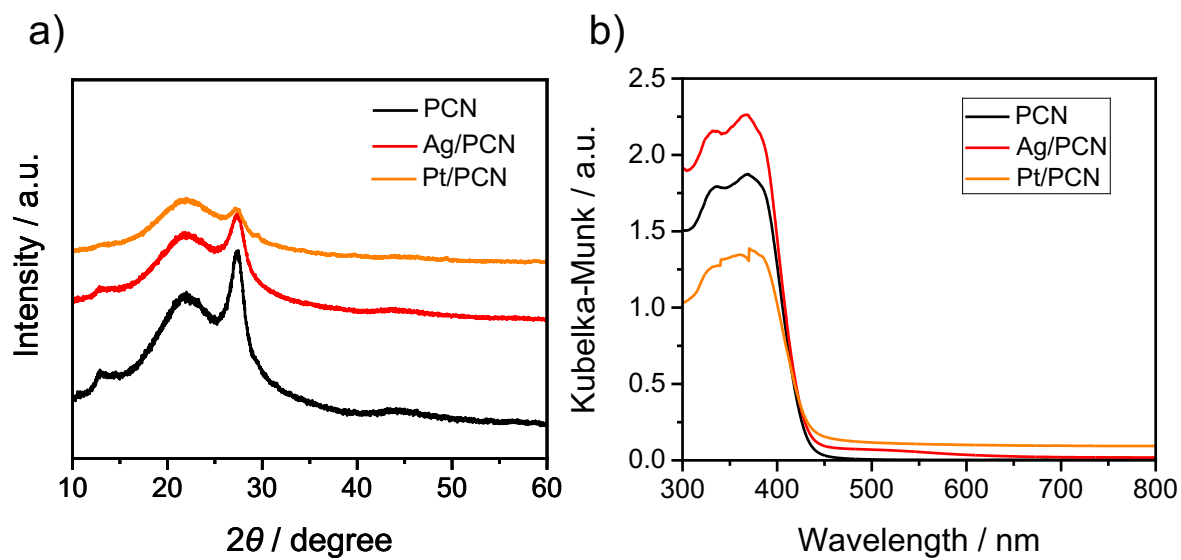


Fig. S1. a) XRD patterns and b) UV-visible diffuse-reflectance spectra for as-prepared PCN, Ag/PCN, and Pt/PCN.

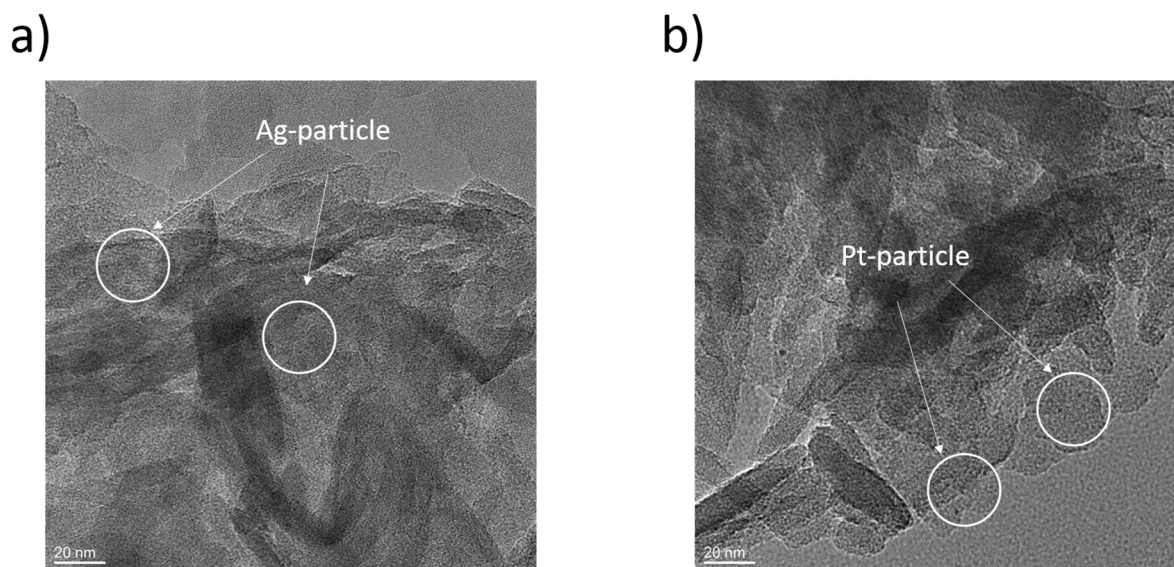


Fig. S2. TEM images of Ag/PCN and Pt/PCN.

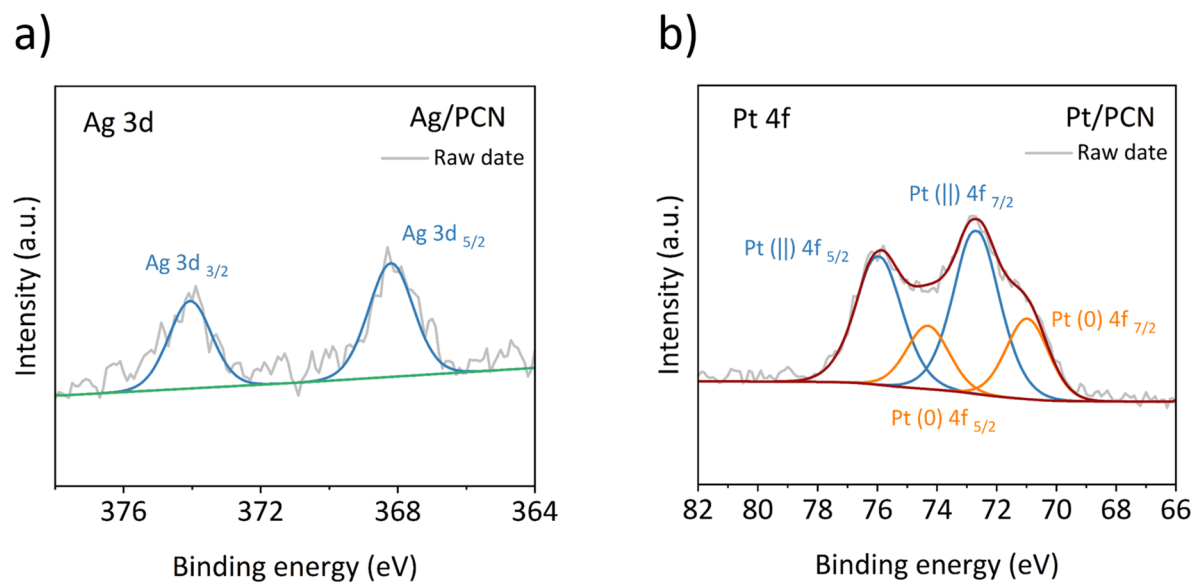


Fig. S3. Ag 3d and Pt 4f XPS spectra of Ag/PCN and Pt/PCN.

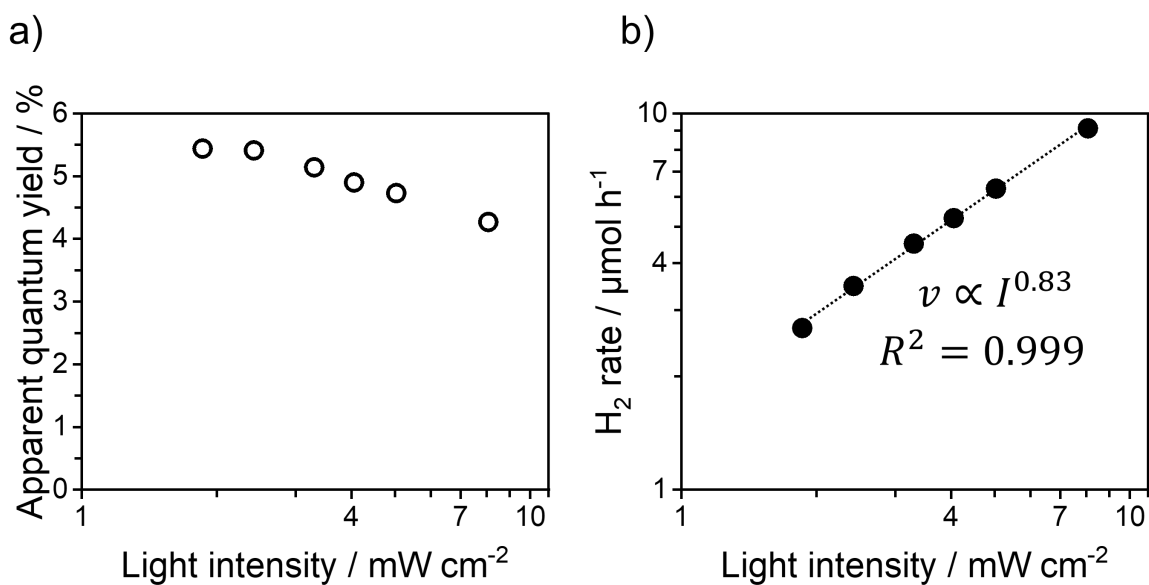


Fig. S4. a) Apparent quantum yield and b) H₂ evolution rate for Pt/PCN as function of incident-light intensity. Reaction conditions: catalyst, 14 mg; reactant solution, DMA:TEOA mixture solvent (4:1 v/v, 14 mL); wavelength of light, 400 nm, Pt: 2.0 wt%.

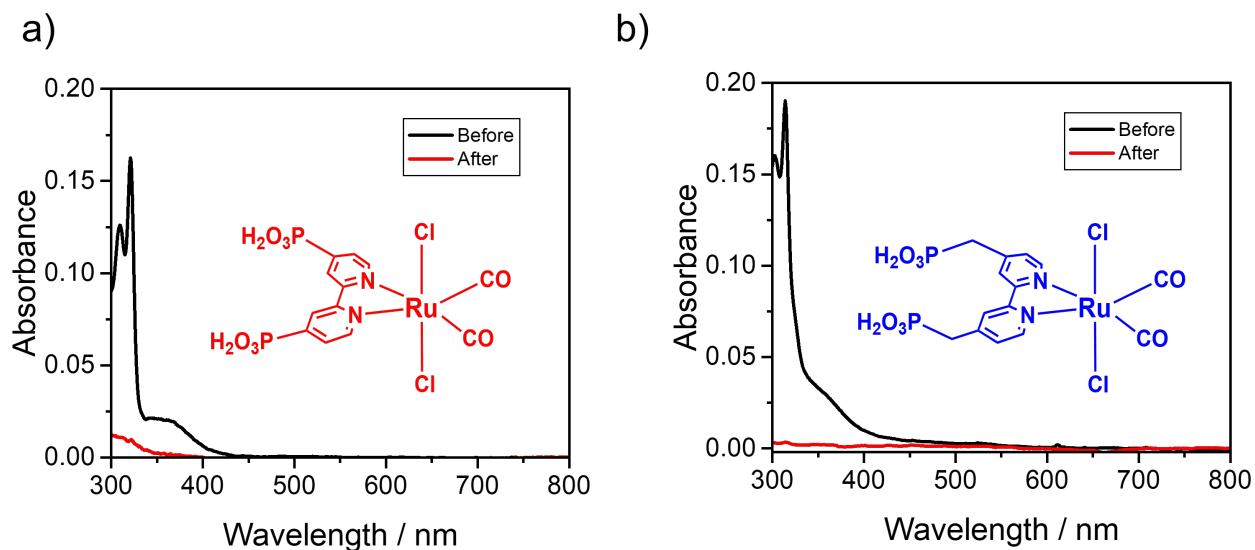


Fig. S5. UV-vis spectra of Ru metal complex in MeOH before and after adsorption: a) RuP and b) RuCP.

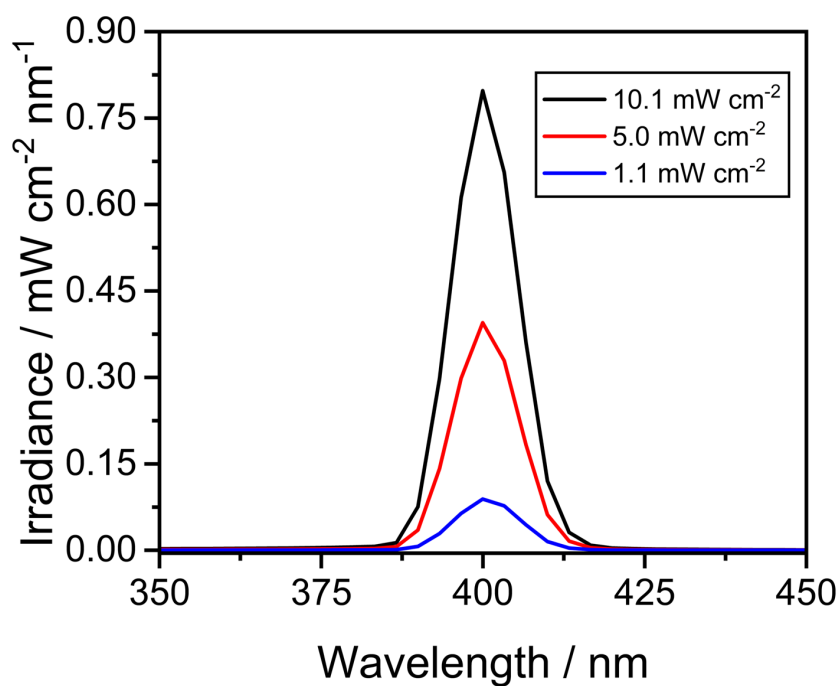


Fig. S6. Spectral irradiance of the monochromatized visible light at 400 nm with different intensities.

Table S1. Numerical data shown in Fig. 1 (**RuP/Ag/PCN**)

Light intensity / mW cm ⁻²	HCOOH rate / μmol h ⁻¹	HCOOH AQY / %	HCOOH selectivity / %	TON _{HCOOH}	H ₂ rate / μmol h ⁻¹	CO rate / μmol h ⁻¹
1.1	0.71	2.43	91	51	0.14	n.d.
1.1	0.75	2.45	95.5	54	0.07	n.d.
2.1	1.34	2.44	95.3	96	0.13	n.d.
4.1	2.56	2.36	95.7	183	0.23	n.d.
5.0	3.11	2.35	95.7	222	0.28	n.d.
6.6	3.22	1.83	94.9	230	0.35	n.d.
8.5	3.43	1.52	91.2	245	0.66	n.d.
8.6	3.14	1.37	90.1	224	0.69	n.d.
10.0	3.18	1.20	94.0	227	0.20	n.d.
10.1	3.12	1.15	86.0	223	0.81	0.21
10.2	4.40	1.63	90.7	314	0.71	0.19

Table S2. Results of data analysis for relationship between rate of HCOOH production (v_{HCOOH}) under 400 nm monochromatized light and incident-light intensity (I)^a

RuP/Ag/PCN				RuCP/Ag/PCN			
Region / mW cm ⁻²	a	b	R^2	Region / mW cm ⁻²	a	b	R^2
1.1–5.0	0.66	0.97	0.999	2.0–10.1	0.76	0.72	0.998
1.1–6.6	0.68	0.89	0.958				
5.0–10.2	2.1	0.23	0.23				

^a Reaction conditions: the same as described in the captions of Figs. 1 and 2. The relationship between v_{HCOOH} and I is analyzed on the basis of the equation $v = aI^b$.

Table S3. Numerical data shown in Fig. 2 (**RuCP/Ag/PCN**)

Light intensity / mW cm ⁻²	HCOOH rate / μmol h ⁻¹	HCOOH AQY / %	HCOOH selectivity / %	TON _{HCOOH}	H ₂ rate / μmol h ⁻¹
2.0	1.21	2.34	89.3	86	0.15
5.0	2.47	1.87	94.4	176	0.15
8.5	3.44	1.53	90.1	244	0.38
10.1	4.01	1.49	92.6	286	0.32

References

1. R. Kuriki, H. Matsunaga, T. Nakashima, K. Wada, A. Yamakata, O. Ishitani and K. Maeda, *J. Am. Chem. Soc.*, 2016, **138**, 5159-5170.
2. M. Shizuno, K. Kato, S. Nishioka, T. Kanazawa, D. Saito, S. Nozawa, A. Yamakata, O. Ishitani and K. Maeda, *ACS Appl. Energy Mater.*, 2022, **5**, 9479-9486.
3. K. Maeda, D. An, C. S. Kumara Ranasinghe, T. Uchiyama, R. Kuriki, T. Kanazawa, D. Lu, S. Nozawa, A. Yamakata, Y. Uchimoto and O. Ishitani, *J. Mater. Chem. A*, 2018, **6**, 9708-9715.
4. P. A. Anderson, G. B. Deacon, K. H. Haarmann, F. R. Keene, T. J. Meyer, D. A. Reitsma, B. W. Skelton, G. F. Strouse and N. C. Thomas, *Inorg. Chem.*, 1995, **34**, 6145-6157.