Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting information

Engineering Covalently Linked NH_2-TiN@PCN-222-Co Single-Atom Photocatalyst for Solar-Driven CO_2-to-CO Conversion

Minh-Khoa Duong,[a] Toan-Anh Quach,[a] Van-Duc Nguyen,[a] Sakar Mohan[b], Trong-On Do[a*]

[a]*Department of Chemical Engineering, Laval University, 1065 Avenue de la Médecine, Quebec, QC G1V0A6, Canada*

[b]*Centre for Nano and Material Sciences, Jain (Deemed-to-be University), Jain Global Campus, Kanakapura road, Bangalore 562112, Karnataka, India.*

**Corresponding Author: Email address: Trong-On.Do@gch.ulaval.ca*

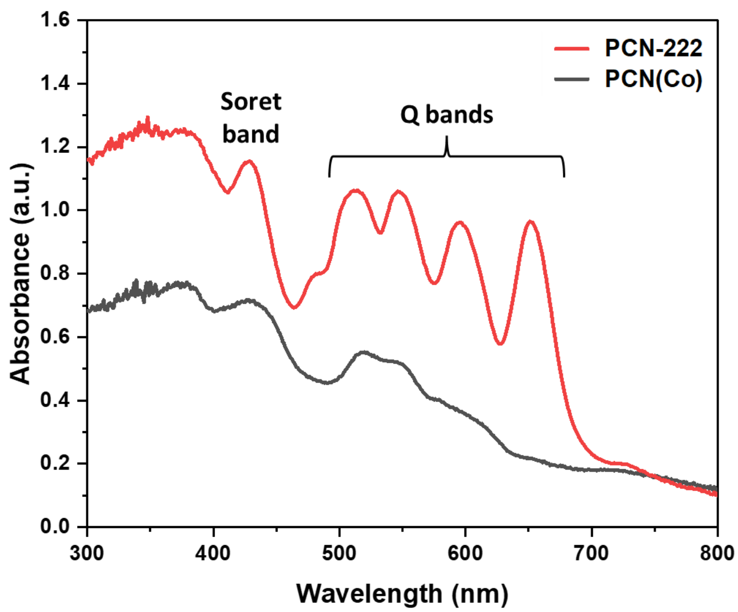


Figure S1. UV-visible absorption spectra of PCN-222 (non-cobalt metalation) and PCN(Co).

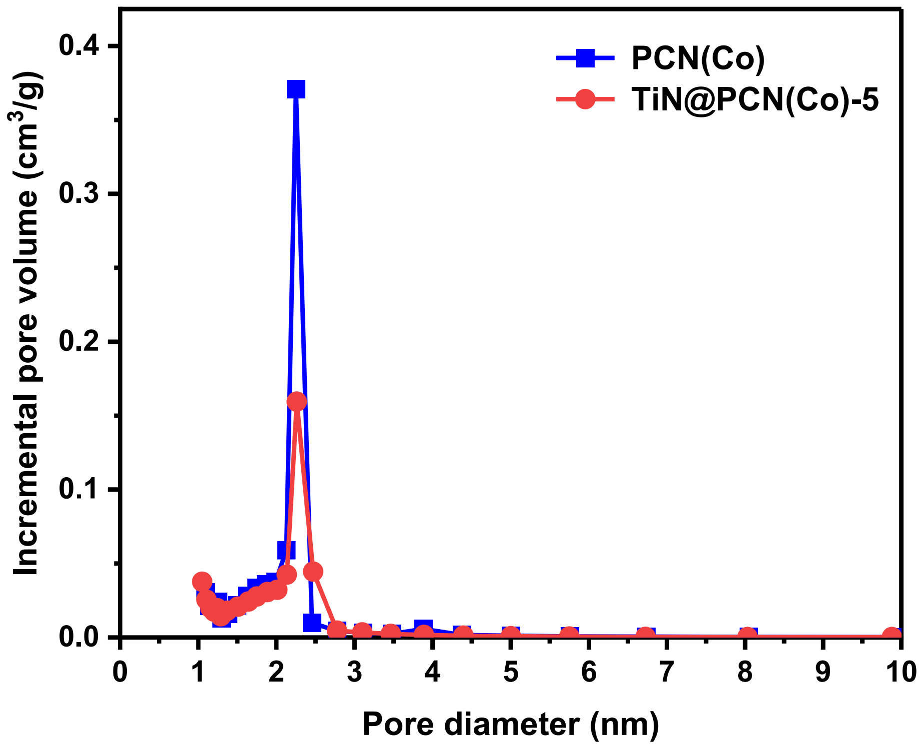


Figure S2. The pore size distribution of PCN(Co) and TiN@PCN(Co)-5

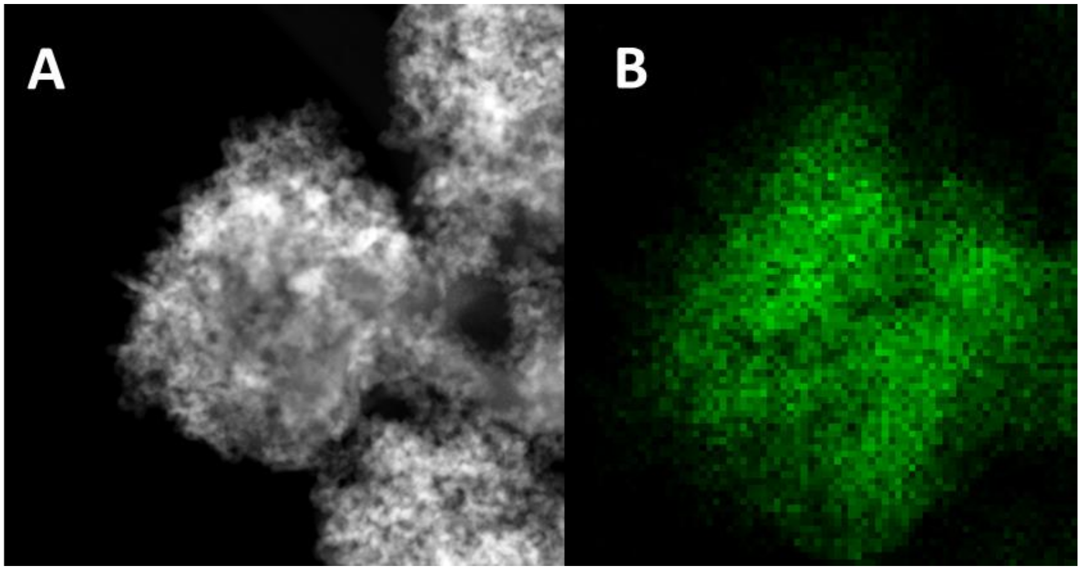
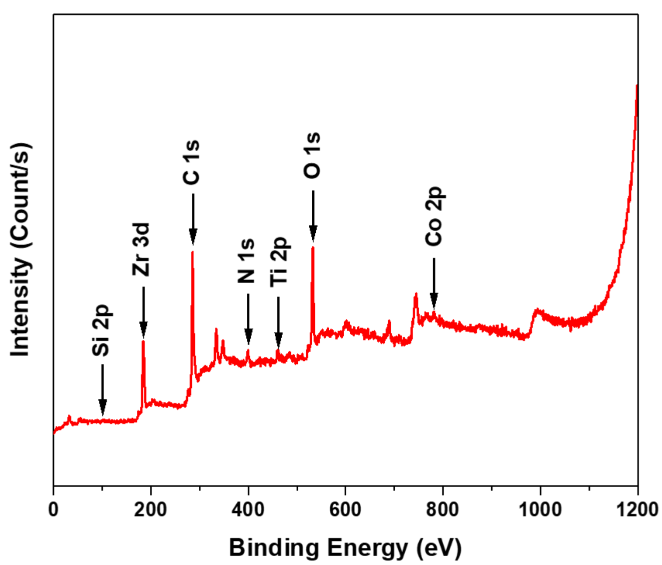


Figure S3. EDS elemental mapping images of (A) full area survey and (B) N K signal of TiN@PCN(Co) sample.



Sample	Atomic %
C 1s	39.57
N 1s	3.41
O 1s	30.35
Co 2p	3.82
Zr 3d	18.94
Ti 2p	3.45
Si 2p	0.45

Figure S4. The survey XPS spectra of TiN@PCN(Co)-5 nanocomposite

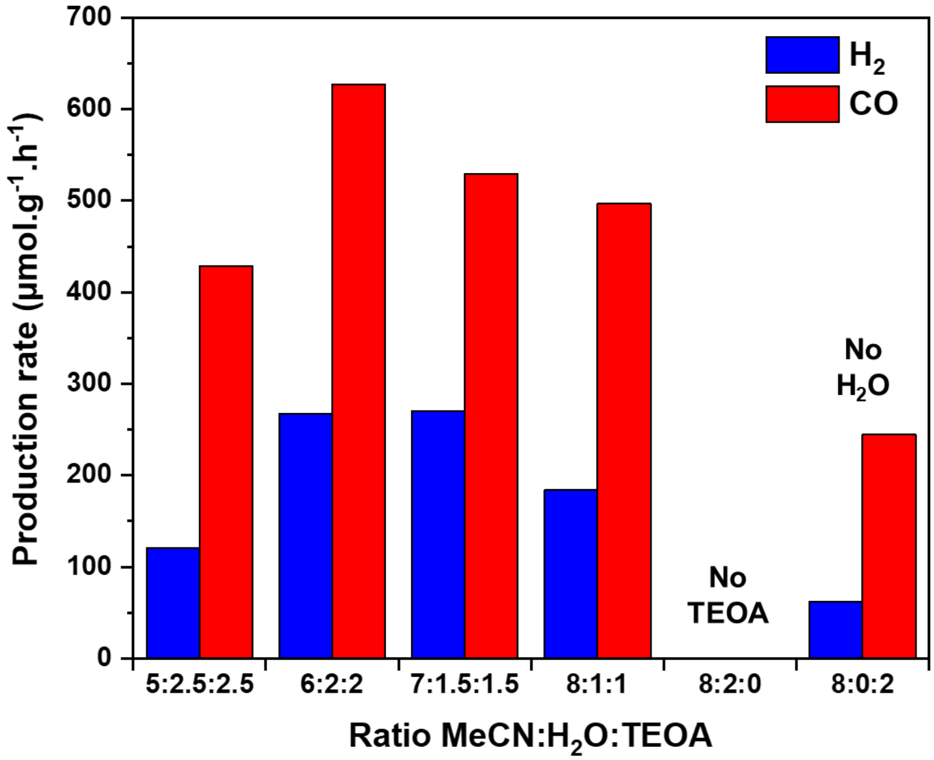


Figure S5. The optimization of solvent ratio MeCN:H_2O:TEOA for the photocatalytic CO_2 reduction

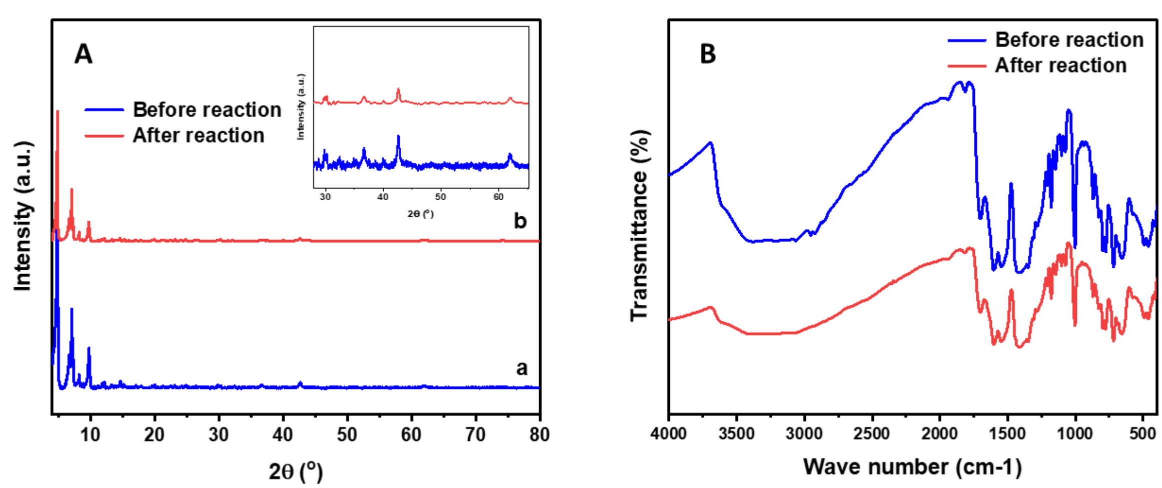


Figure S6. (A) XRD spectra and (B) FT-IR spectra of TiN@PCN(Co)-5 before and after 5 cycle stability test.

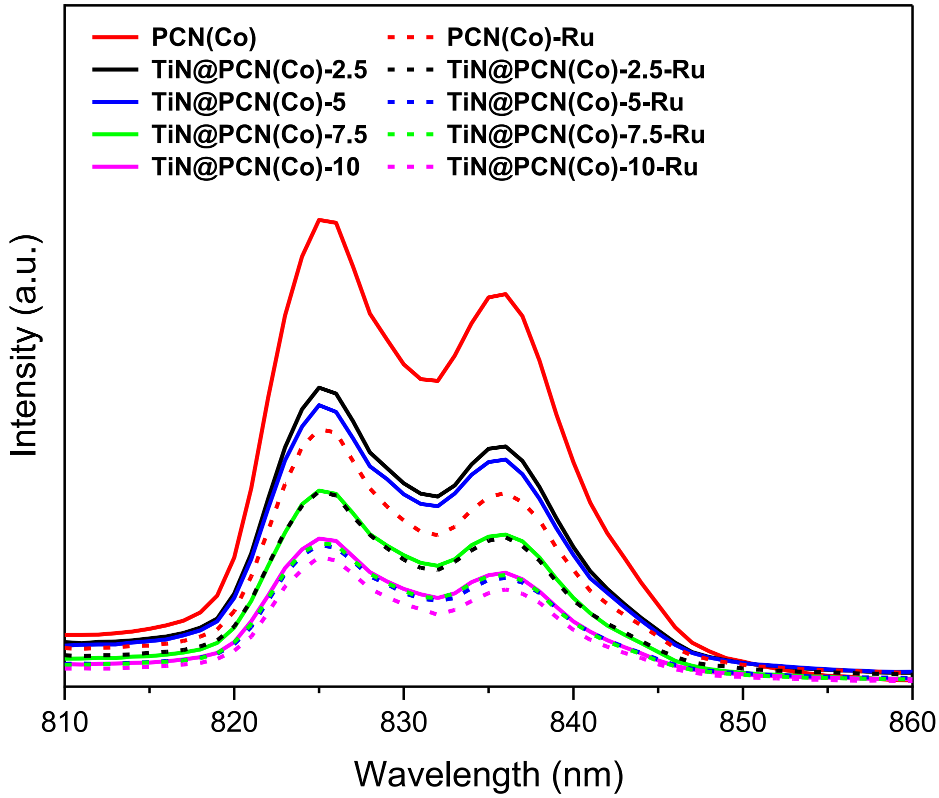


Figure S7. Photoluminescence spectra of bare PCN(Co) and TiN@PCN(Co)-x samples with and without photosensitizer $[Ru(bpy)_3]Cl_2.6H_2O$.

Table S1: The fitting circuit parameters of electrodes.

Sample	**PCN(Co)**	**TiN@PCN-2.5**	**TiN@PCN-5**	**TiN@PCN-7.5**	**TiN@PCN-10**
R_s (Ω)	15.14	14.31	17.44	16.44	19.68
Q (x 10^{-5})	5.27	5.38	5.54	5.95	5.58
R_{ct} (Ω)	6391	3958	2742	5473	4249

Table S2: Fit parameter of TRPL curves for the bare PCN(Co) and TiN@PCN(Co)-x composites with and without the presence of photosensitizer.

Sample	τ_1/ns	A_1 (%)	τ_2/ns	A_2 (%)	τ_3/ns	A_3 (%)	T_{av}/ns
PCN(Co)	1.22	37.3	1.83	37.4	2.44	25.3	1.885
PCN(Co)-Ru	1.39	16.8	2.09	41.6	2.79	41.6	2.375
TiN@PCN-2.5	1.43	34.3	2.14	35.5	2.86	30.2	2.268
TiN@PCN-2.5-Ru	1.53	37.0	2.30	34.6	3.07	28.4	2.403
TiN@PCN-5	1.50	35.4	2.25	34.0	3.00	30.6	2.378
TiN@PCN-5-Ru	1.53	40.6	2.30	20.1	3.07	39.3	2.494
TiN@PCN-7.5	1.18	37.1	1.78	34.2	2.37	28.7	1.859
TiN@PCN-7.5-Ru	1.39	35.0	2.09	30.6	2.79	34.4	2.248
TiN@PCN-10	1.60	53.0	2.40	47.0	3.21	0.0	2.060
TiN@PCN-10-Ru	1.39	34.9	2.09	34.6	2.79	30.5	2.213

The average lifetime is calculated by the following equation:

$$\tau_{av} = \frac{(A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)}{(A_1\tau_1 + A_2\tau_2 + A_3\tau_3)}$$

Table S3: Comparison of photocatalytic CO_2 reduction activities with the reported photocatalyst in the literature

Catalyst	Light source	Co-Catalyst	Sacrificial agent	Photosensitizer	CO Production rate (µmol. $g^{-1}.h^{-1}$)	References
TiN@PCN-222-Co	**150 W Xe lamp**	**No**	**TEOA**	**$[Ru(bpy)_3]Cl_2.6H_2O$**	**627.42**	**This work**
gC_3N_4/PCN-222(Fe^{III})	300 W Xe lamp	No	No	No	28.5	[1]
CdS@PCN-222-Co	150 W Xe lamp	No	TEOA	$[Ru(bpy)_3]Cl_2.6H_2O$	636.41	[2]
PCN-222(Pt)/BiOCl	300 W Xe lamp	No	No	No	8.38	[3]
PCN-224(Cu)/TiO_2	300 W Xe lamp	No	No	No	37.21	[4]

References

1. Zhou, D., et al., *Construction of local coordination environment of iron sites over g-C_3N_4/PCN-222 (Fe) composite with high CO_2 photoreduction performance.* Applied Catalysis B: Environment and Energy, 2024. **344**: p. 123639.
2. Quach, T.-A., M.-K. Duong, S. Mohan, and T.-O. Do, *Single Cobalt Atom-Integrated Z-Scheme CdS@ PCN-222 Heterojunction for Enhanced Syngas Production from Solar-Driven CO_2 Reduction.* Energy & Fuels, 2025.
3. Li, L., et al., *Construction of PCN-222 (Pt)/BiOCl heterojunction with built-in electric field drive charge separation for enhanced photocatalytic performance.* Applied Surface Science, 2025. **697**: p. 162978.
4. Wang, L., et al., *Integration of copper (II)-porphyrin zirconium metal–organic framework and titanium dioxide to construct Z-scheme system for highly improved photocatalytic CO2 reduction.* ACS Sustainable Chemistry & Engineering, 2019. **7**(18): p. 15660-15670.