Supporting Information

Single-Atom Pt-N_3 Sites on the Stable Covalent Triazine Framework Nanosheets for Photocatalytic N_2 Fixation

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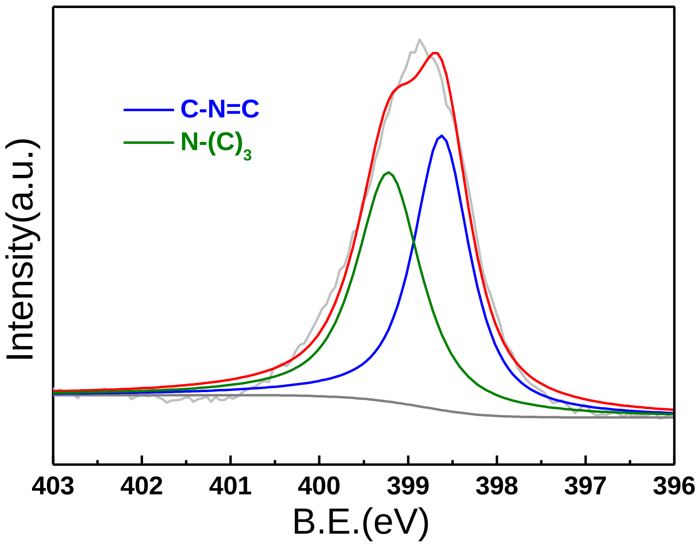


Figure S1. N 1s XPS spectra of CTF-PDDA-TPDH.

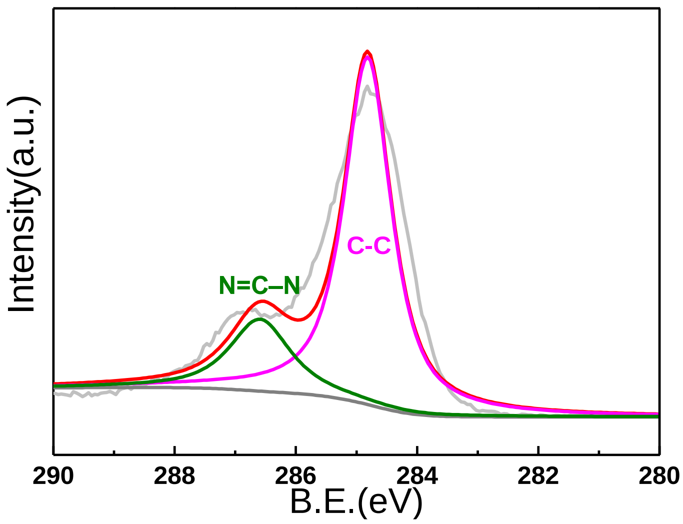


Figure S2. C 1s XPS spectra of CTF-PDDA-TPDH.

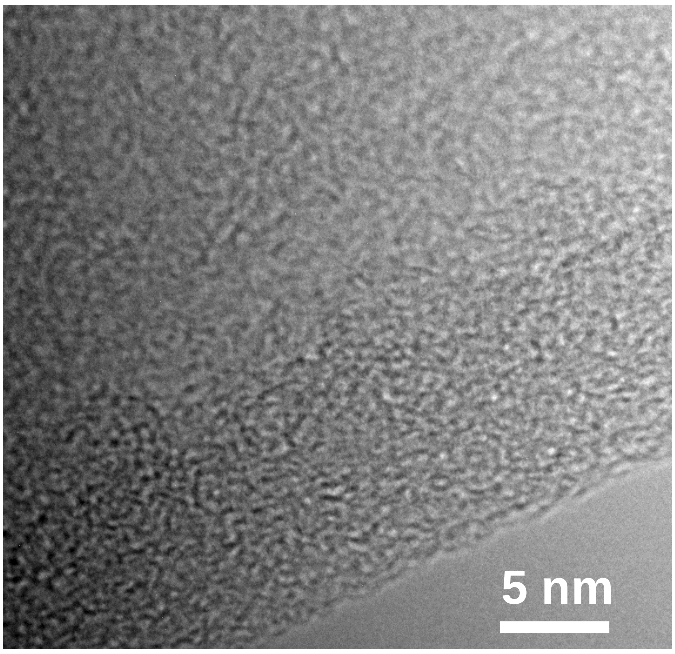


Figure S3. HR-TEM images of CTF-PDDA-TPDH.

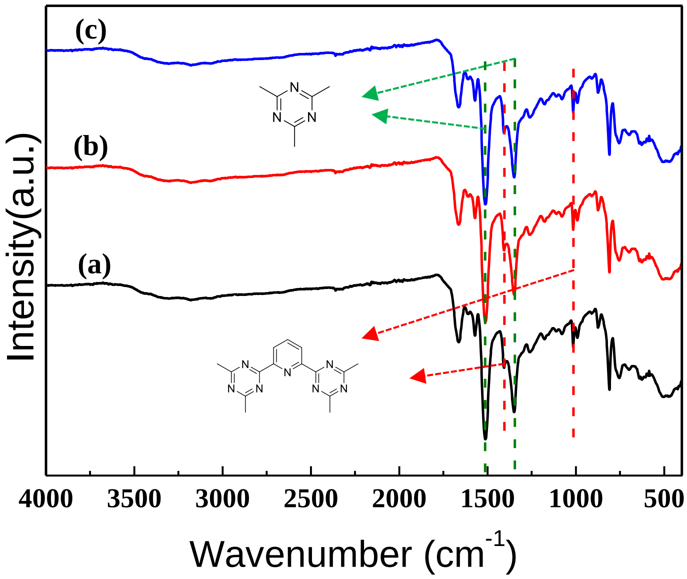


Figure S4. FT-IR spectra of (a) CTF-PDDA-TPDH and CTF-PDDA-TPDH with (b) 1 M HCl and (c) 1 M NaOH treatment.

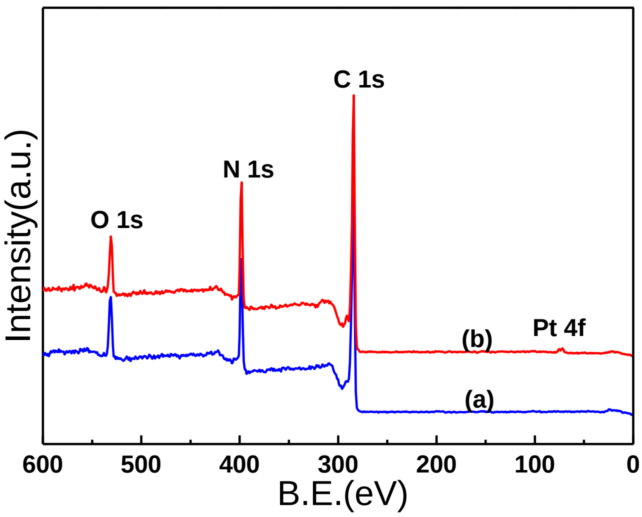


Figure S5. XPS full spectra of (a) CTF-PDDA-TPDH and (b) Pt-SACs/CTF.

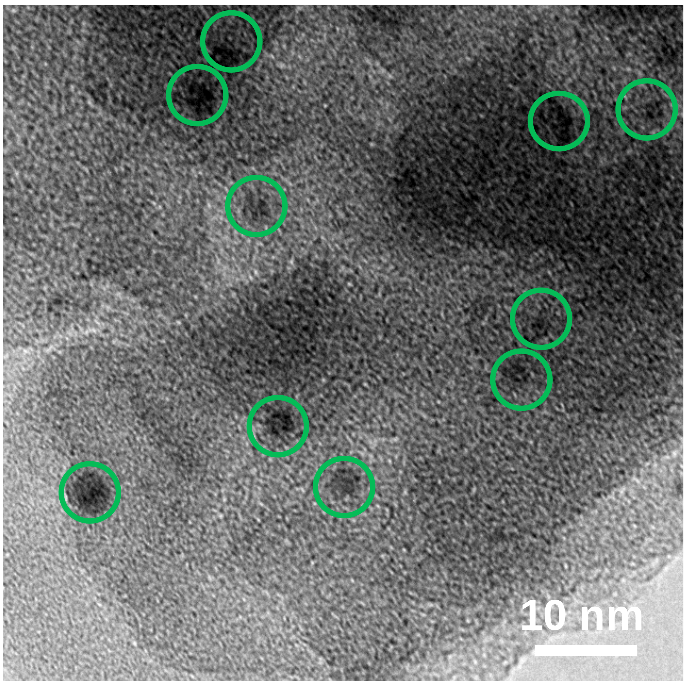


Figure S6. HR-TEM image of Pt-NPs/CTF.

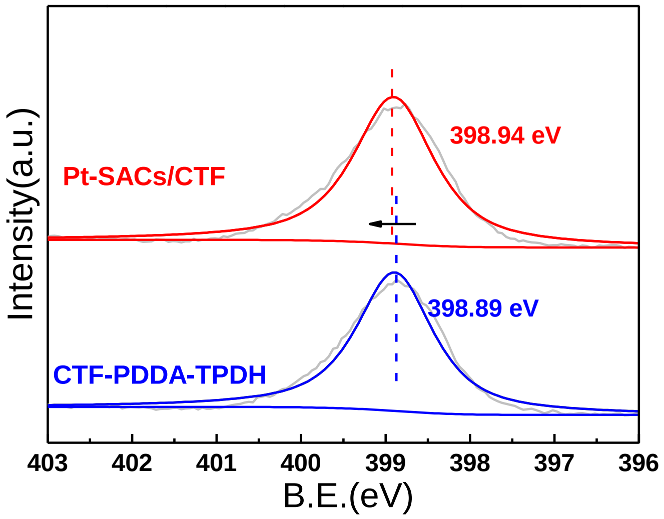


Figure S7. N 1s XPS spectra of CTF-PDDA-TPDH and Pt-SACs/CTF.

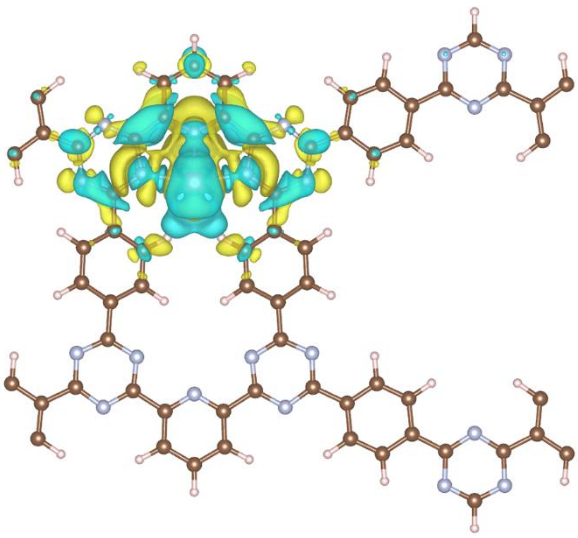


Figure S8. The charge density difference of the Pt atom anchored on the N_3 site of CTF, in which the level of the isosurface is chosen to be 0.001 e Å^{-3}. The cyan and yellow areas indicate electron depletion and accumulation, respectively.

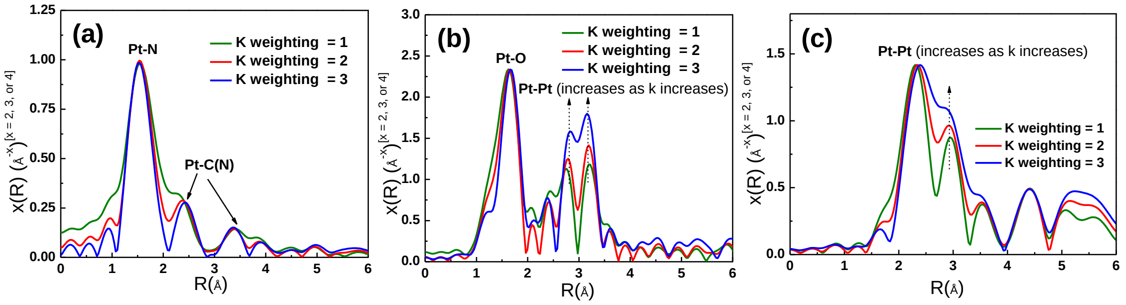


Figure S9. The k^1-, k^2-, and k^3-weighted Pt L_3-edge EXAFS χ(R) spectra of (a) Pt-SACs/CTF, (b) PtO_2 reference, and Pt foil reference.

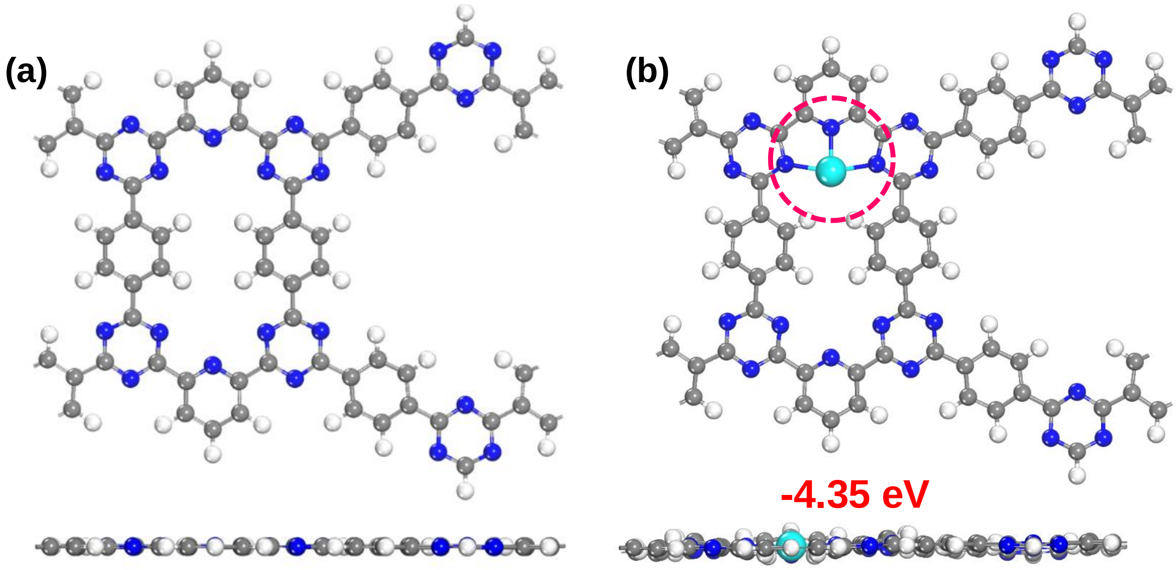


Figure S10. Top and side view of the structures of (a) CTF-PDDA-TPDH and (b) Pt-SACs/CTF. Carbon, nitrogen, platinum, and hydrogen atoms are depicted in black, blue, cyan, and white, respectively.

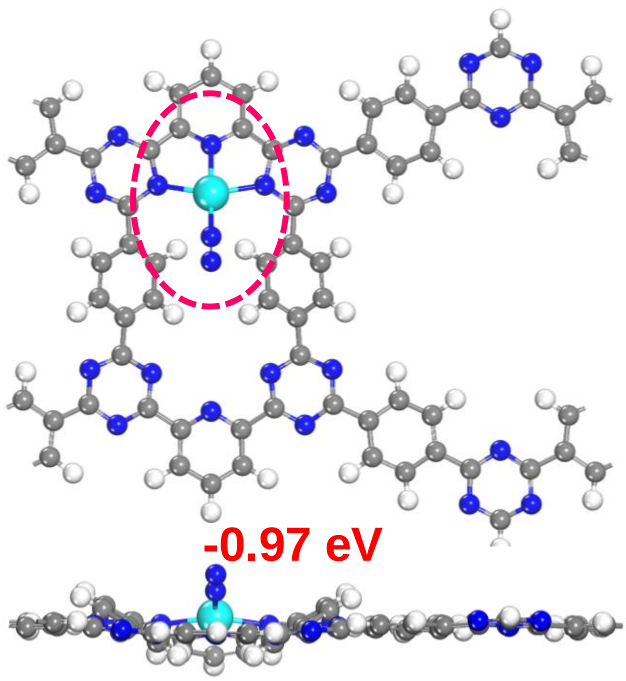


Figure S11. Top and side view of the structures of the adsorption energy between N_2 and Pt-SACs/CTF. Carbon, nitrogen, platinum, and hydrogen atoms are depicted in black, blue, cyan, and white, respectively.

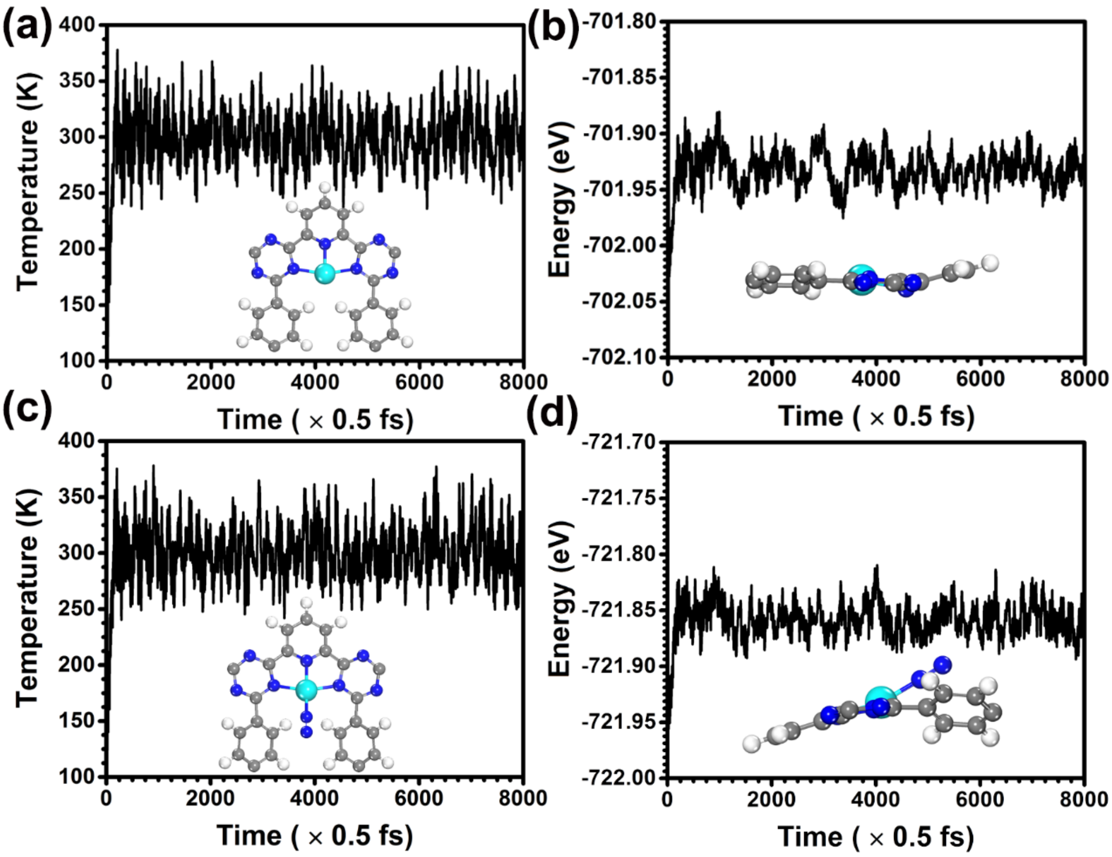


Figure S12. Variations of (a) temperature and (b) energy against the time for the *ab initio* molecular dynamics simulations of Pt-SACs/CTF. Variations of (c) temperature and (d) energy against the time for the *ab initio* molecular dynamics simulations of N_2-Pt-SACs/CTF. Inserts are top and side views of the snapshot of atomic configurations. For Pt-SACs/CTF and N_2-Pt-SACs/CTF, the simulation is run under 300 K for 4 ps with a time step of 0.5 fs, respectively.

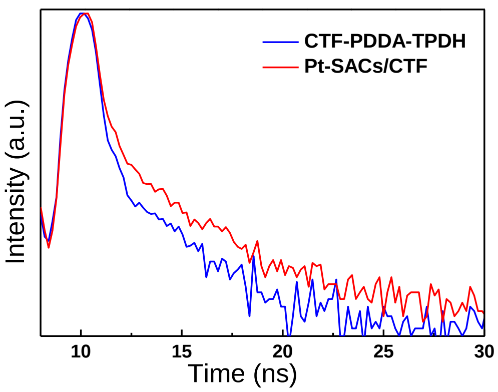
Table S1. Structural parameters of Pt-SACs/CTF extracted from the FT-EXAFS fitting.

Sample	Path	C.N.	R (Å)	$\sigma^2\times10^3$ (Å^2)	ΔE (eV)	R factor
Pt foil	Pt-Pt	12*	2.76	3.8	0.8	0.006
Pt-SACs/CTF	Pt-N	3	2.02	4.7	14.1	0.008

*C.N. is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatter distances); ΔE is edge-energy shift. R factor is used to value the goodness of the fitting. The fitting of k weighting is 2. The fitting range of Pt foil is 1-3.3 Å at R space and 2-10 Å at k space. The fitting range of Pt-SACs/CTF is 1-3 Å at R space and 3-9 Å at k space.

Table S2. A comparison of the corresponding bond length of Pt-N by EXAFS fitting and DFT calculations.

Sample	Method	Pt-N (Å)
$Pt-N_3$	EXAFS fitting	2.02
	DFT calculations	2.02/2.07/2.07



Samples	τ_1 (ns)	τ_2 (ns)
CTF-PDDA-TPDH	0.11	1.11
Pt-SACs/CTF	0.14	1.48

Figure S13. Time-resolved fluorescence decay spectra of CTF-PDDA-TPDH and Pt-SACs/CTF.

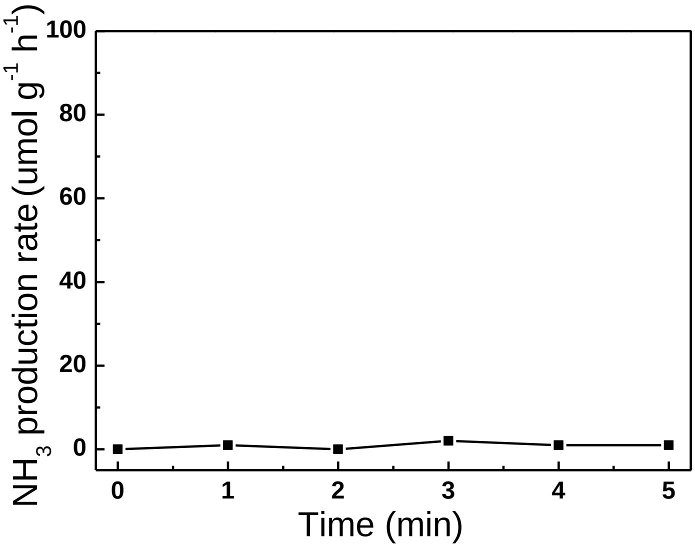


Figure S14. Quantitative determination of NH_4^+ generated of Pt-SACs/CTF in argon atmospheres.

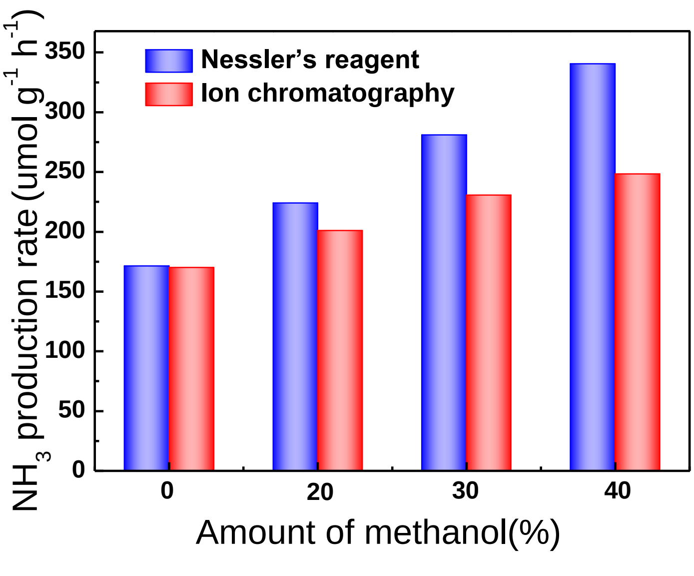


Figure S15. Nessler's reagent and Ion chromatography results of Pt-SACs/CTF with different amount of methanol.

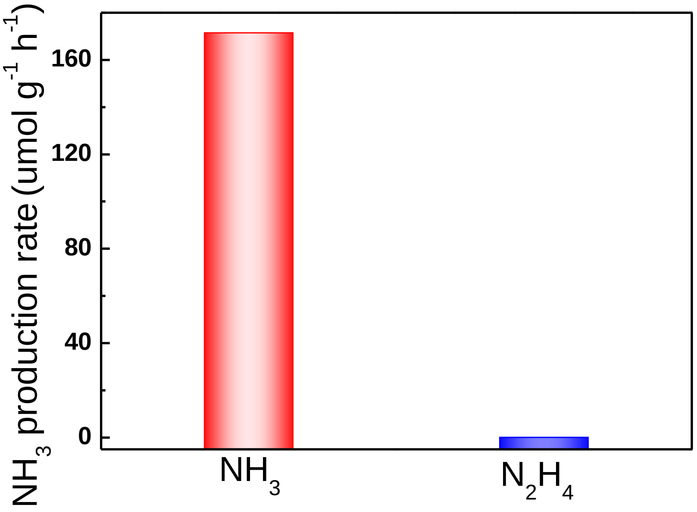


Figure S16. Quantitative determination of N_2H_4 generated over Pt-SACs/CTF.

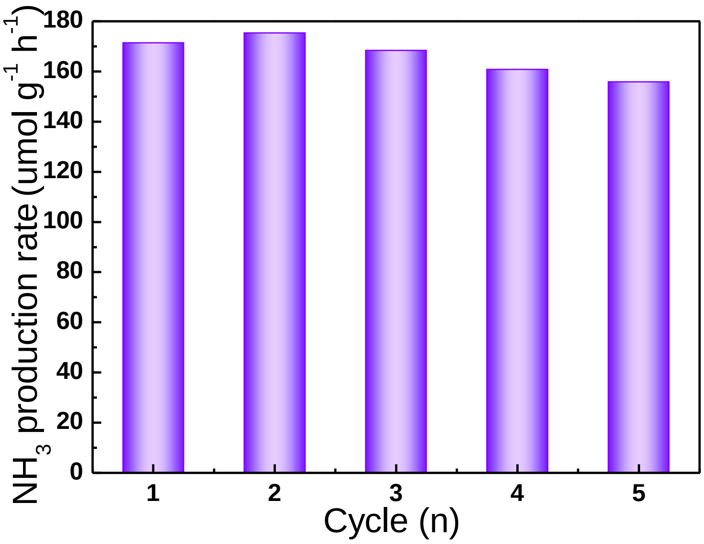


Figure S17. Quantitative determination of NH_4^+ generated of Pt-SACs/CTF in five consecutive cycles.

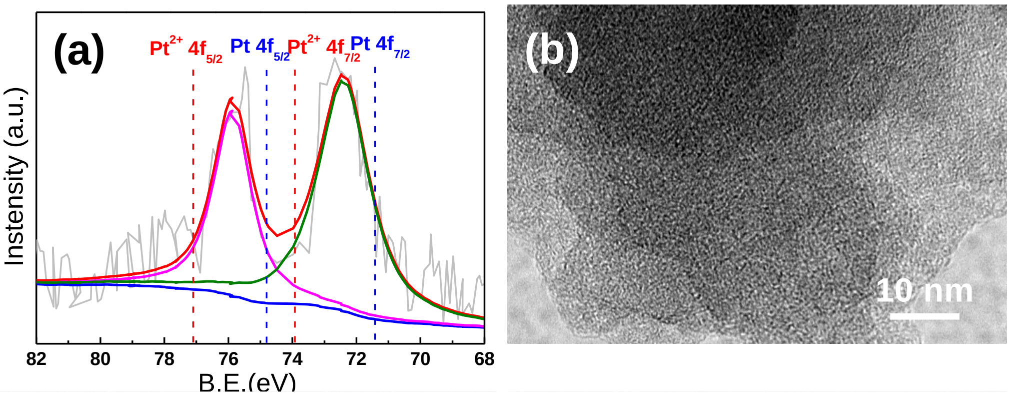


Figure S18. (a) The Pt 4f XPS spectra, (b) HR-TEM

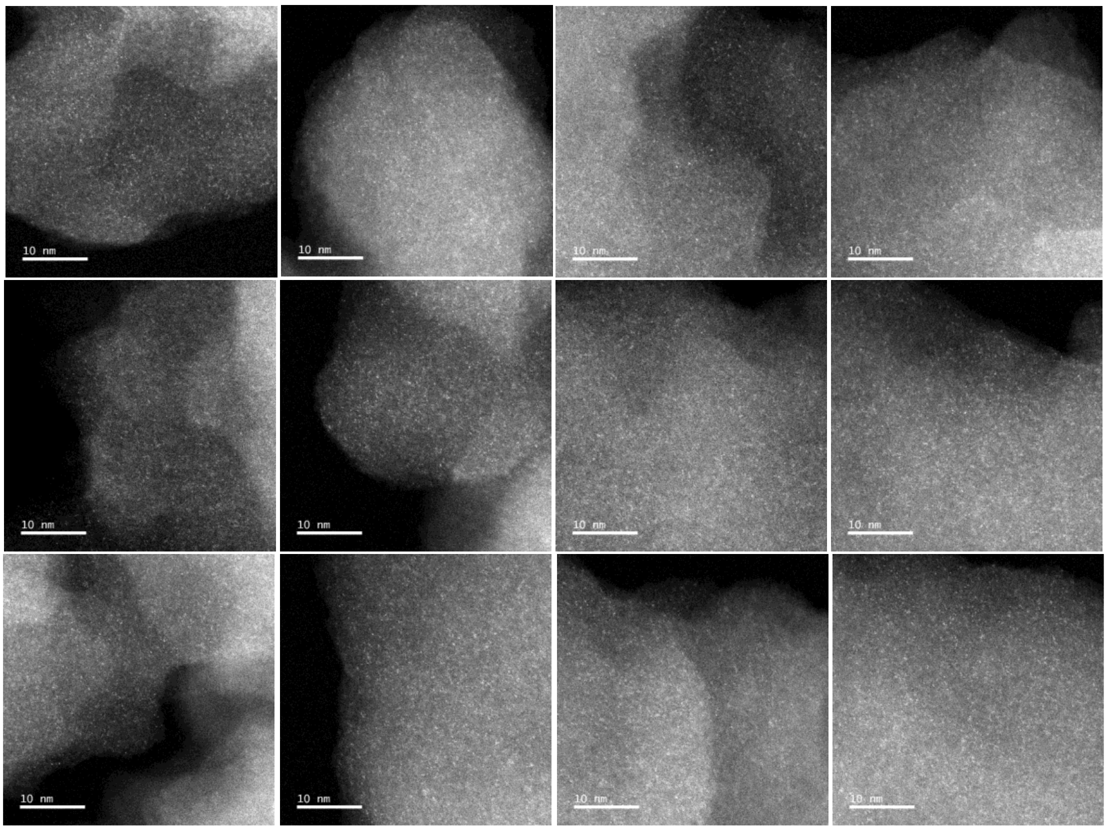


Figure S19. HADDF-STEM images of Pt-SACs/CTF after five cycles.

Table S3. Photocatalytic N_2 fixation over the photocatalysts without scavenger under various reaction conditions.

Catalyst	Scavenger	Light Source	Ammonia generation rate (μmol/h/g)	Reference
Pt-SACs/CTF	No	300 W Xenon lamp,780 nm>λ>420 nm	171.40	This work
Bi_5O_7Br nanotubes	No	300 W Xenon lamp, λ>400 nm	1380	1
BiO quantum dots	No	500 W Xenon lamp	1226	2
WO_3-600	No	300 W Xenon lamp, λ>400 nm,	132	3
BP5	No	300 W Xenon lamp,λ>420 nm	160	4
BiOBr of oxygen vacancies	No	300 W Xenon lamp,λ>420 nm	104.2	5
TiO_2 of oxygen vacancies	No	300 W Hg lamp, λ>280 nm	9	6
Fe-doped TiO_2	No	360 W Hg-Arc Lamp, Full Spectrum	11.5	7
Pt-TiO_2	No	100 W high-pressure mercury lamp, Full Spectrum	9.3	8
Pt-$SrTiO_3$	No	100 W high-pressure mercury lamp, Full Spectrum	8.0	
Pt-CdS	No	100 W high-pressure mercury lamp, Full Spectrum	16.3	
$Fe_2O_3(H_2O)_n$	No	100 W tungsten filament lamp, Full Spectrum	0.56	9
Ru/TiO_2	No	150 W Xe arc lamp, Full Spectrum	29.4	10
Fe_2O_3	No	150 W Xe lamp, Full Spectrum	10.0	11

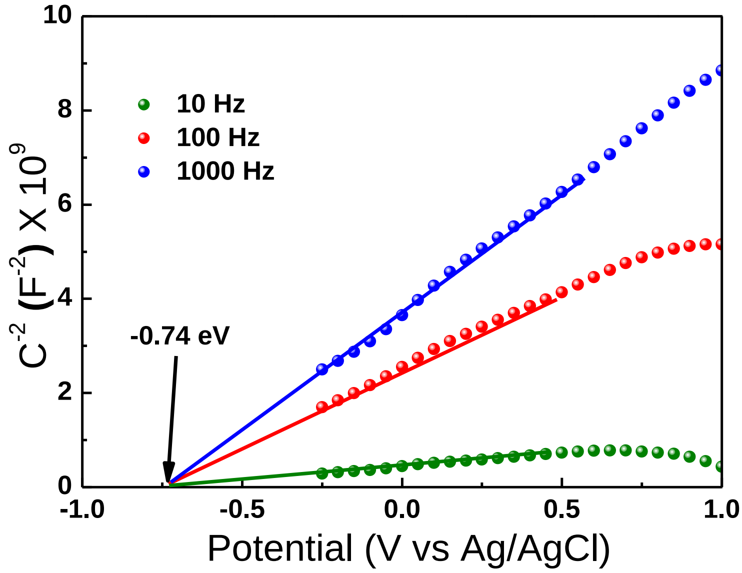


Figure S20. Mott−Schottky plots of CTF-PDDA-TPDH electrodes in 0.5 M Na_2SO_4 aqueous solution (0.1 M) at 10, 100 and 1000 Hz.

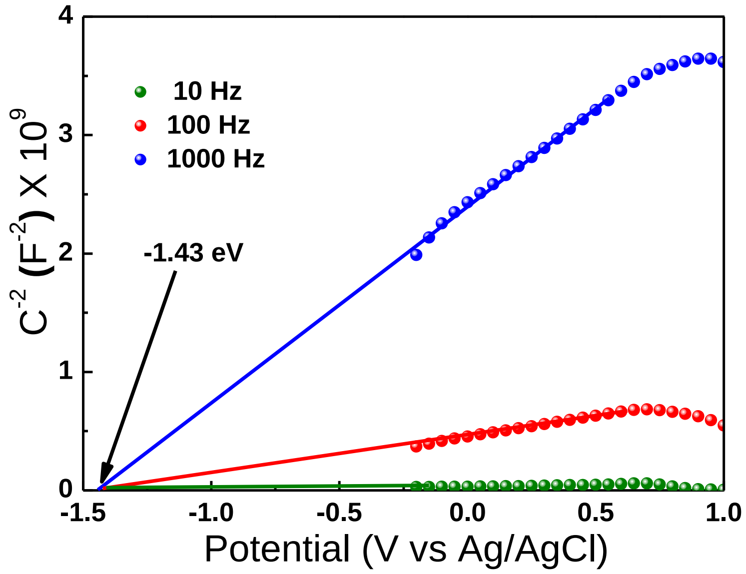


Figure S21. Mott−Schottky plots of Pt-SACs/CTF electrodes in 0.5 M Na_2SO_4 aqueous solution at 10, 100 and 1000 Hz.

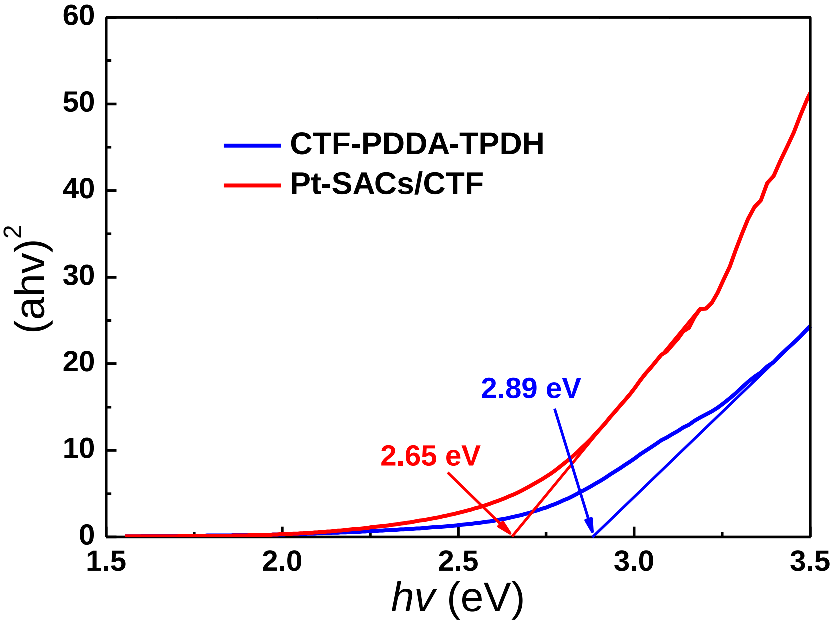


Figure S22. The plots of (ahv)$^{1/2}$ vs photon energy (hv) of CTF-PDDA-TPDH and Pt-SACs/CTF.

Reference

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