Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Band gap engineering of structured microporous graphitic carbons by N doping and its influence on the photocatalytic overall water splitting

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Supplementary information

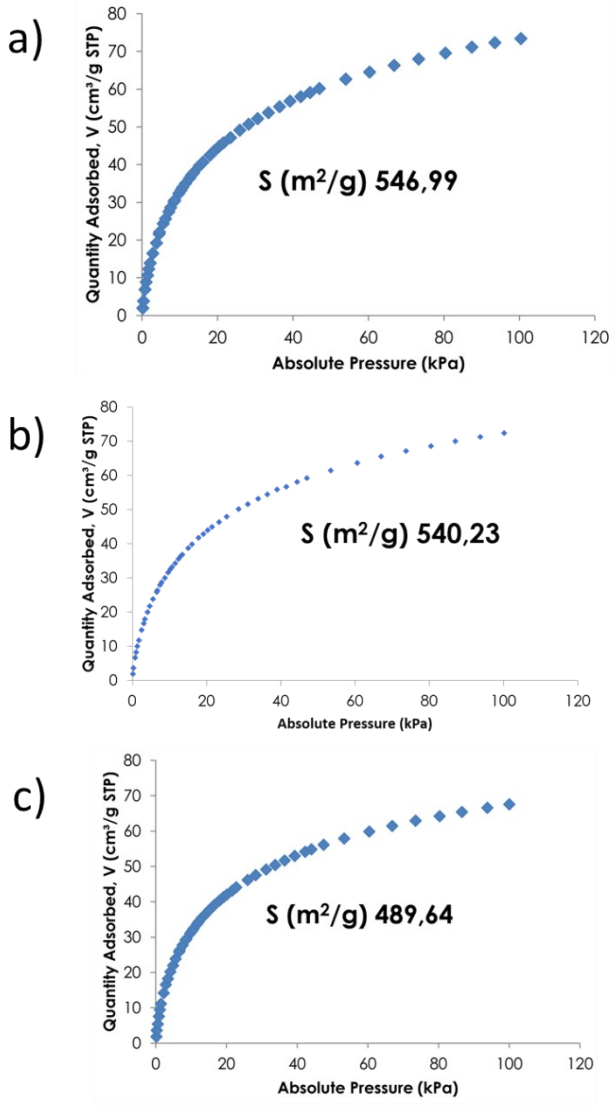
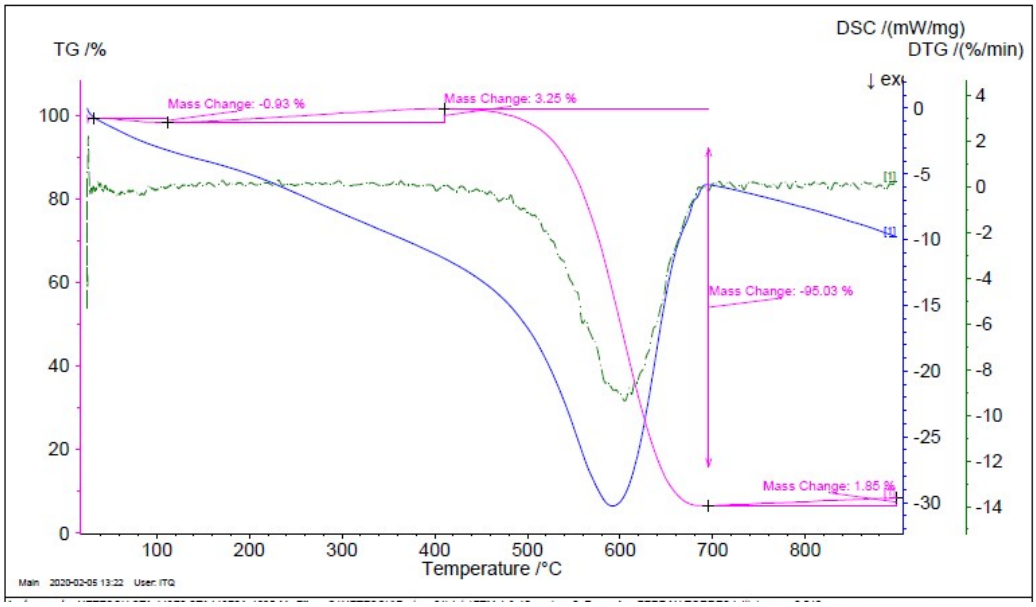


Figure S1. CO_2 adsorption plot of a) (N)C_α-1 b) (N)C_α-2 and c) (N)C_α-3.



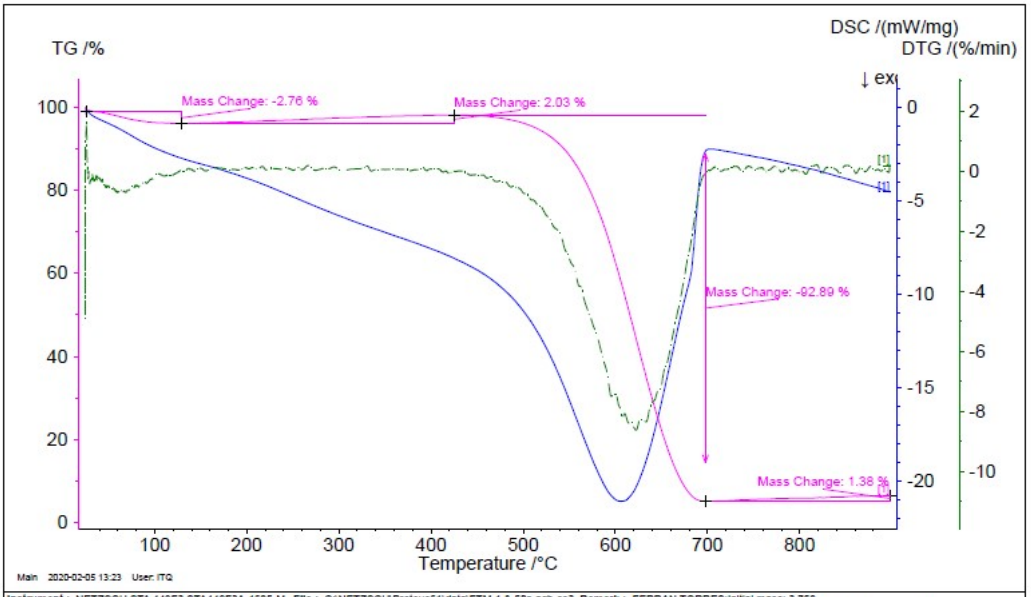


Figure S2. Thermogravimetric analysis of (N)C_{α}-1.

Figure S3. Thermogravimetric analysis of (N)C_{α}-2.

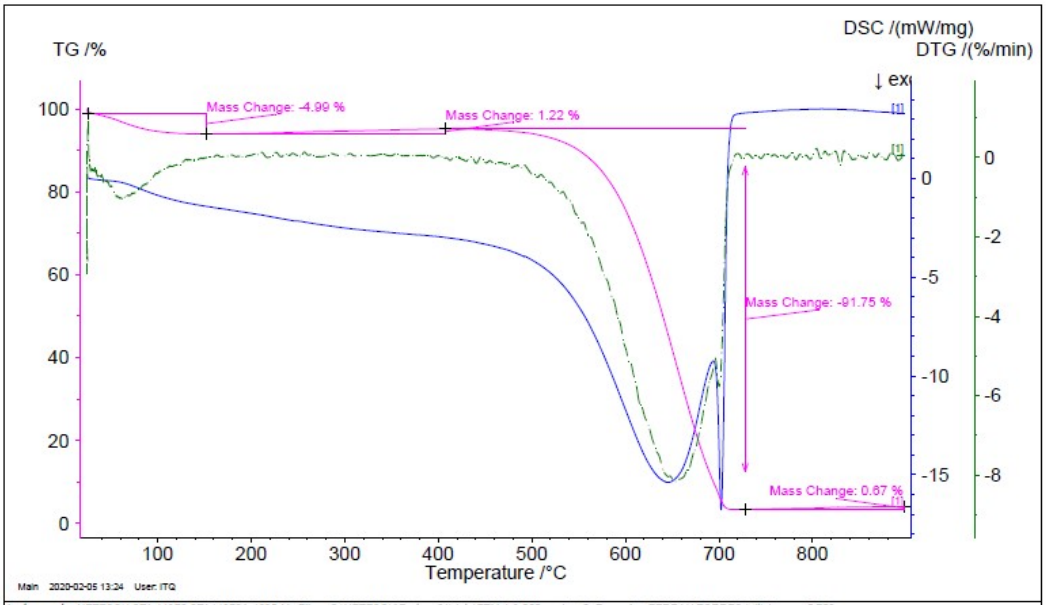


Figure S4. Thermogravimetric analysis of (N)C_{α}-3.

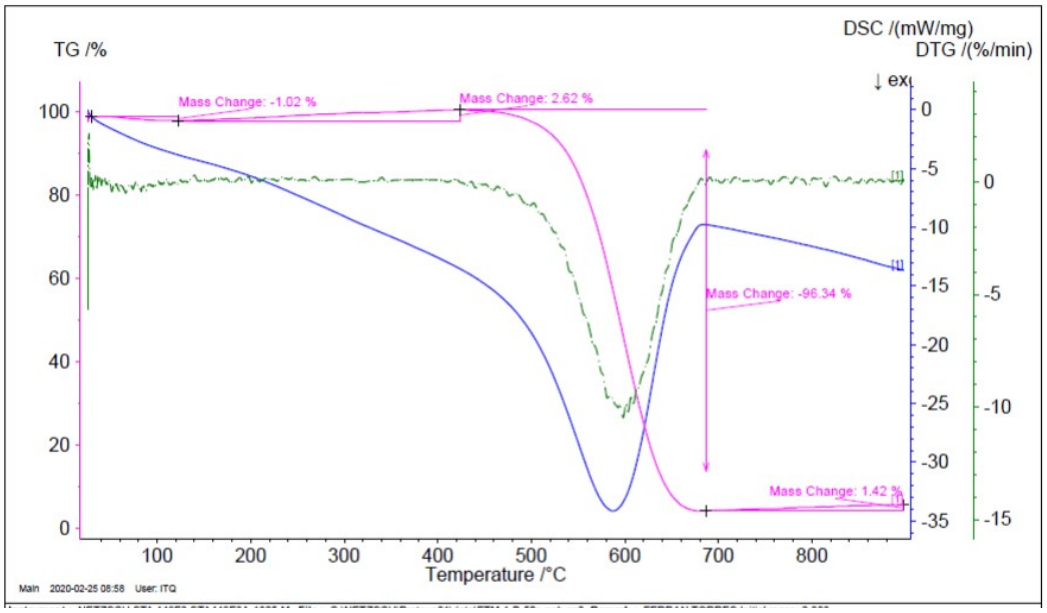


Figure S5. Thermogravimetric analysis of (N)C_{β}.

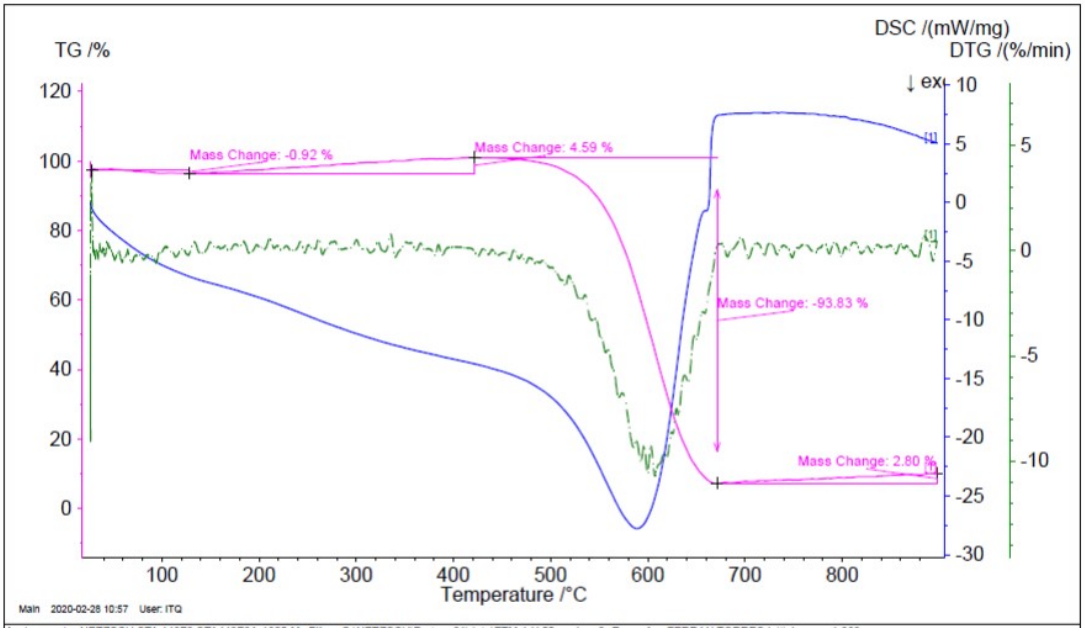


Figure S6. Thermogravimetric analysis of (N)C_γ.

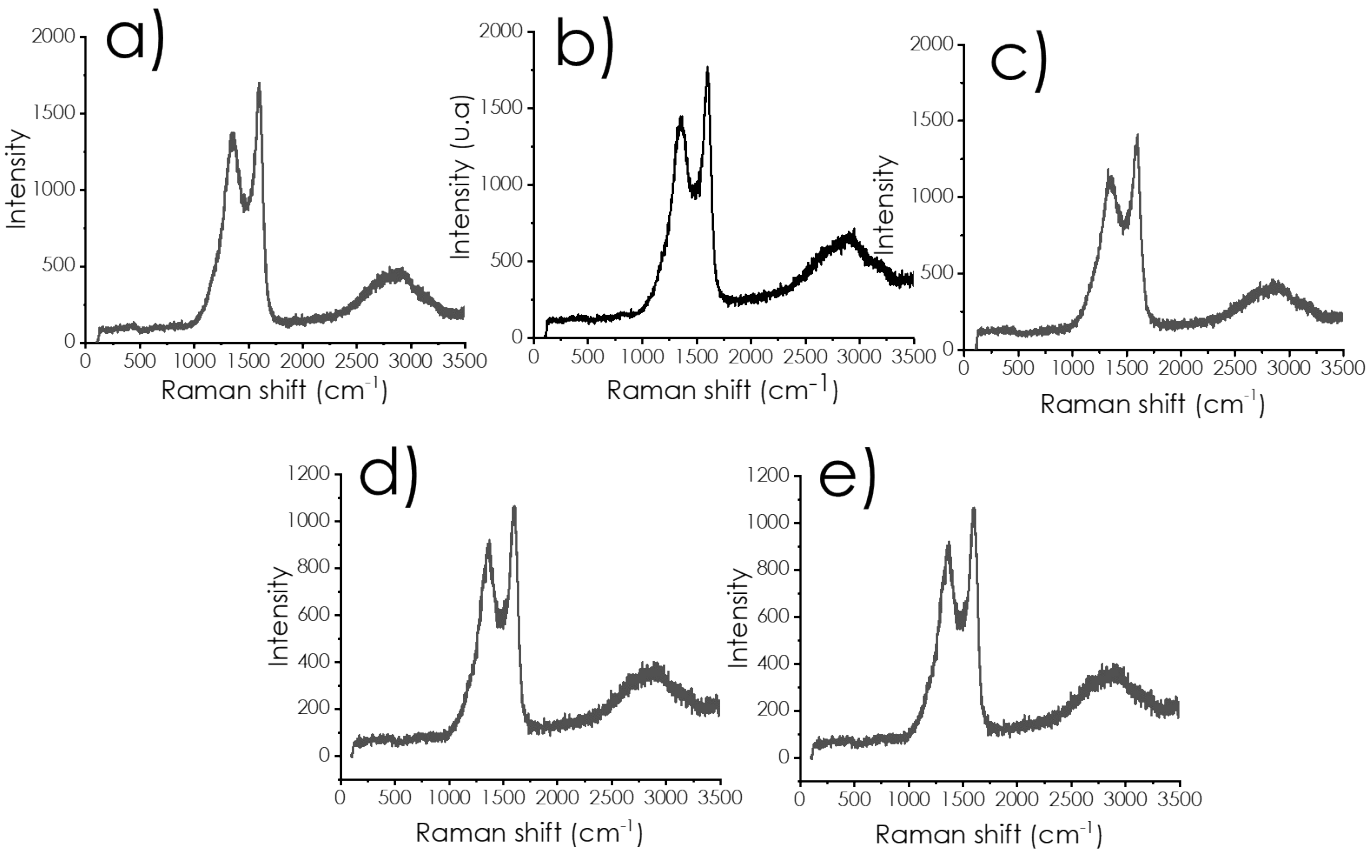


Figure S7. Raman spectra of a) (N)C_α-1, b) (N)C_α-2, c) (N)C_α-3, d) (N)C_β and e) (N)C_γ.

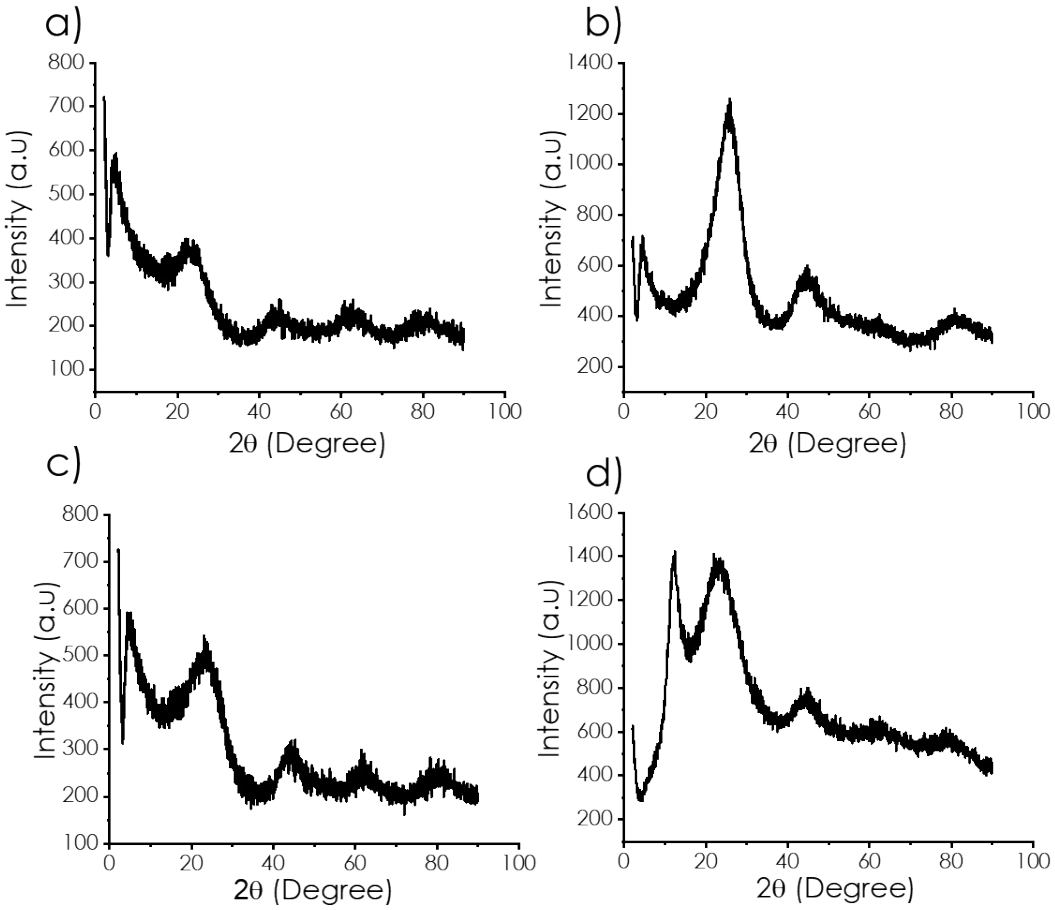


Figure S8. XRD of a) (N)C_{α}-1, b) (N)C_{α}-3, c) (N)C_{β} and d) (N)C_{γ}.

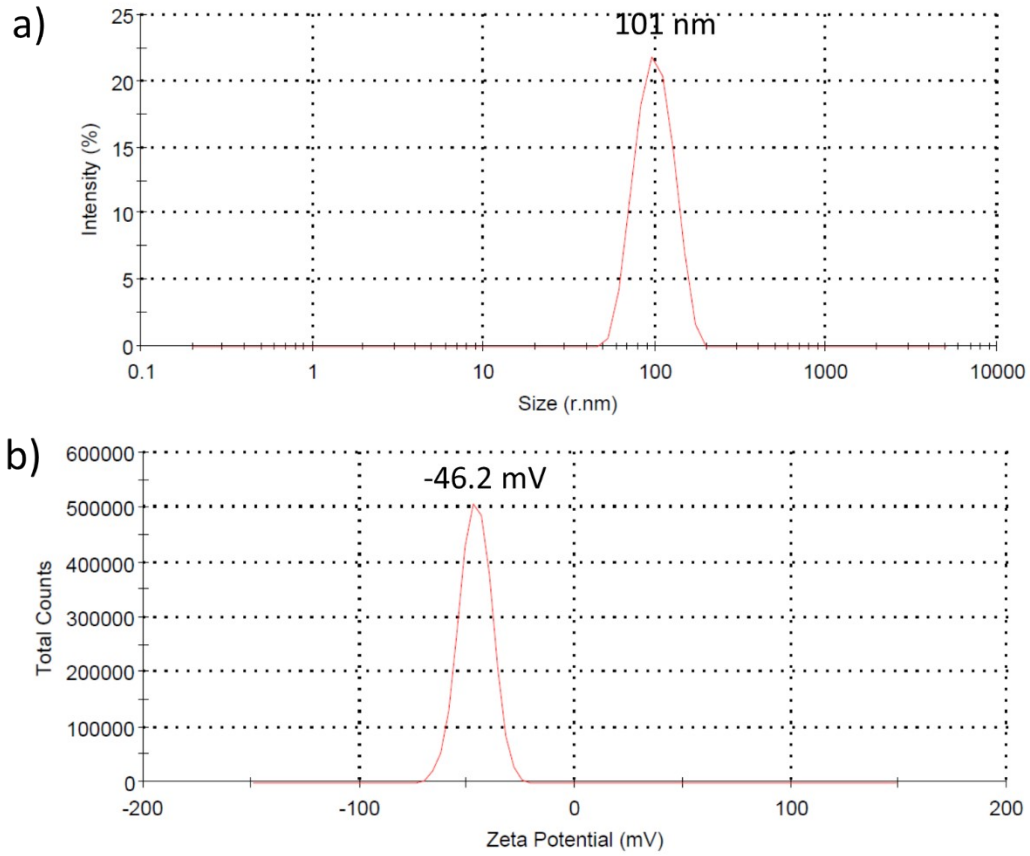


Figure S9. Particle size distribution and Zeta potential of aqueous suspensions of (N)C_{α}-2.

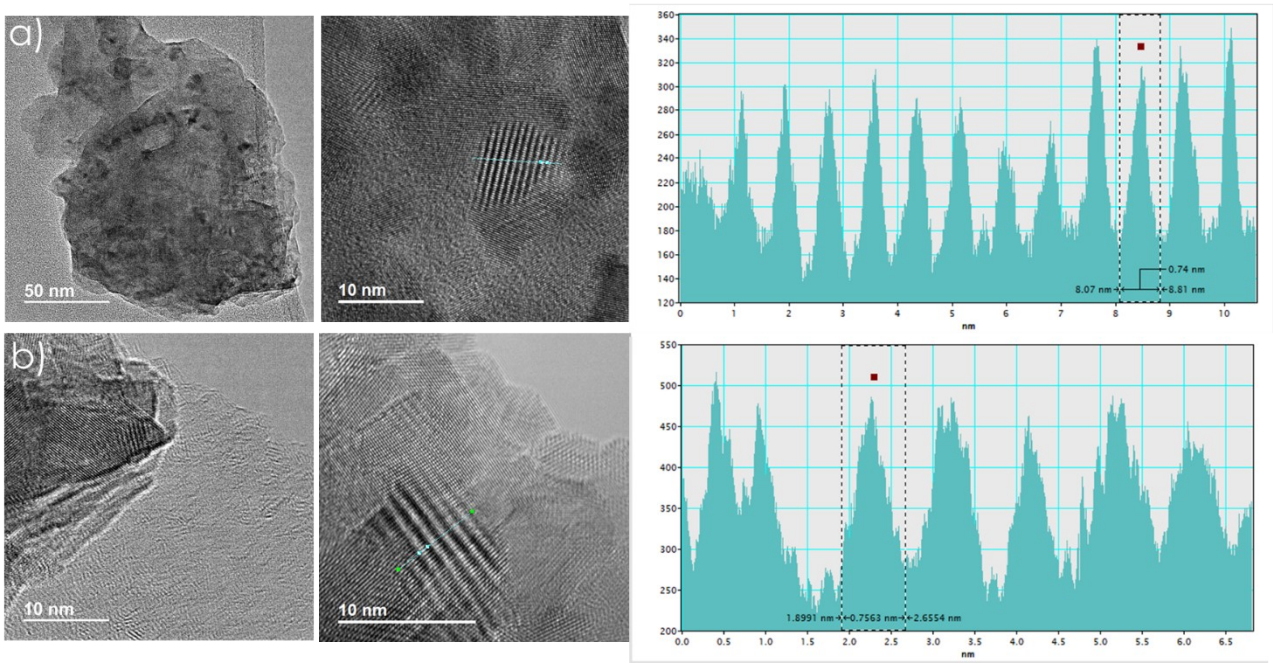


Figure S10. TEM images and the periodic contrast across the blue line of the TEM images of the samples a) (N)C_β and b) (N)C_γ.

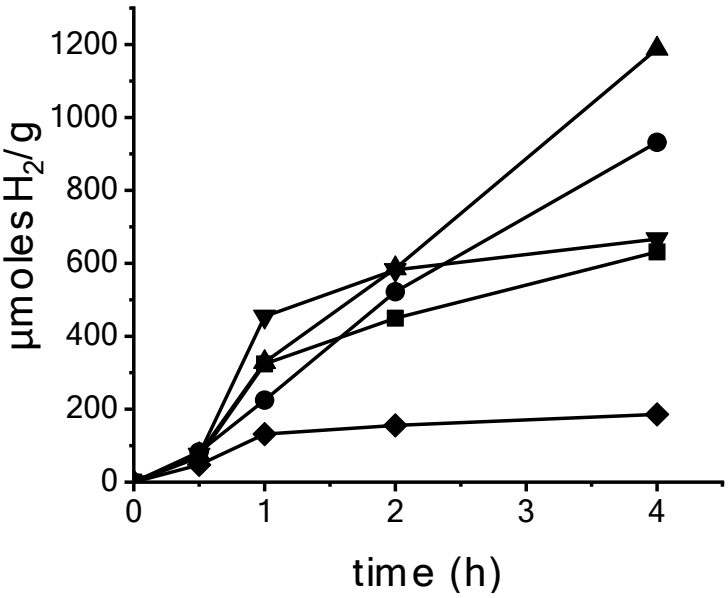


Figure S11. Temporal profiles of hydrogen evolution using as photocatalyst (N)C_α-2 at different temperatures: ▼ 40 ºC, ● 50 ºC, ▲ 60 ºC, ■ 65 ºC and 70 ºC.

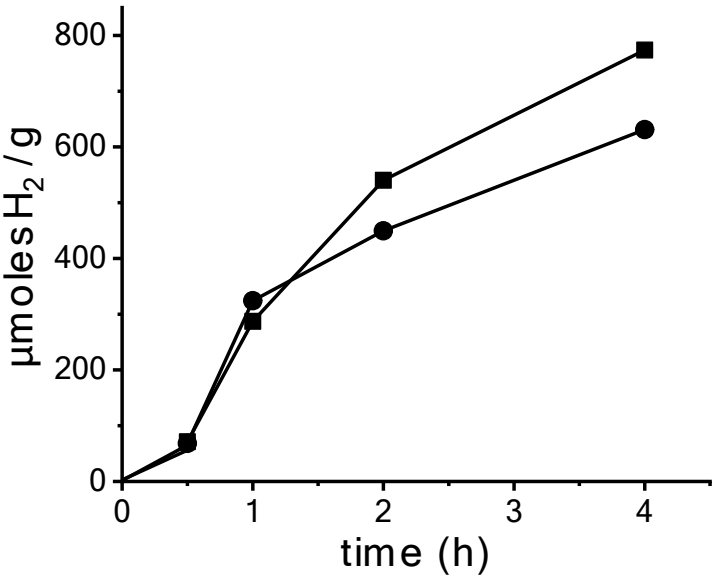


Figure S12. Temporal profiles of hydrogen evolution using as photocatalyst (N)C_{α}-2 in the presence of ●) methanol or ■) triethanolamine as sacrificial agent.

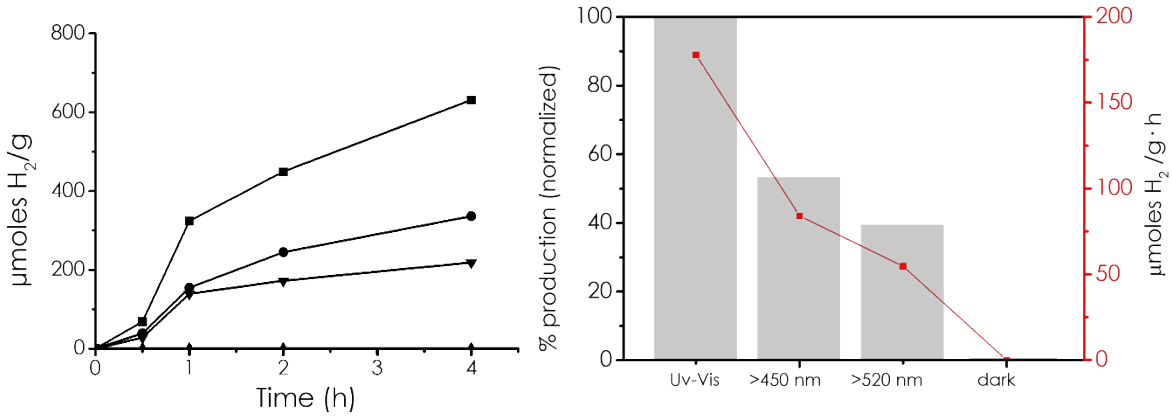


Figure S13 Left) Temporal profiles of hydrogen evolution using as photocatalyst (N)C_a-2 and irradiated with: ■ UV-VIS, ● >450 nm, ▼ >520 nm, ▲ dark. Right) Bar diagram of the relative H_2 production as a function of the irradiation wavelength.

Calculation of valence band edge. The valence band spectrum was first calibrated by C1s (284.5 eV). The valence band edge position was determined by an intersection of tangent line and baseline of the valence band low energy absorption peak and the obtained value refers to the valence band energy versus to Fermi level, E_v^f.

versus NHE:

$$E_v^{NHE} = E_v^f + (\phi sp - 4{,}44) = 1{,}444 \text{ eV}$$

Versus Vacuum:

$$E_v^{Vacuum} = E_v^f + \phi sp = 5{,}880 \text{ eV}$$

Where is the valence band energy versus NHE, is the valence band energy versus E Fermi NHE E_v^f level and ϕsp is the work function of the Spectrometer (4.244 eV).

Calculation of conduction band

Bgap= 2.007 eV

versus NHE:

$$ECB = EVB - Bgap = -0.763 \text{ eV}$$

Versus Vacuum:

$$ECB = EVB - Bgap = 3.677 \text{ eV}$$

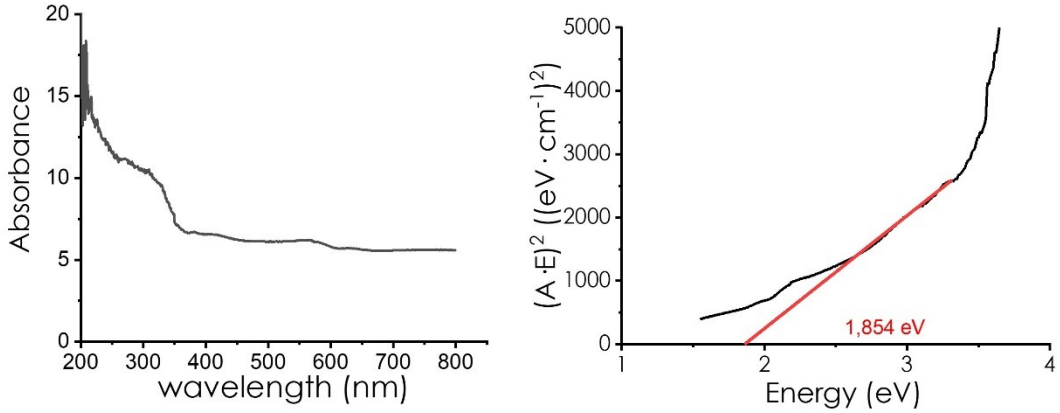


Figure S14. a) UV-Vis absorption spectrum of (N)C_a-1. b) Optical bandgap (N)C_a-1 obtained from the Tauc plot of (N)C_a-1..

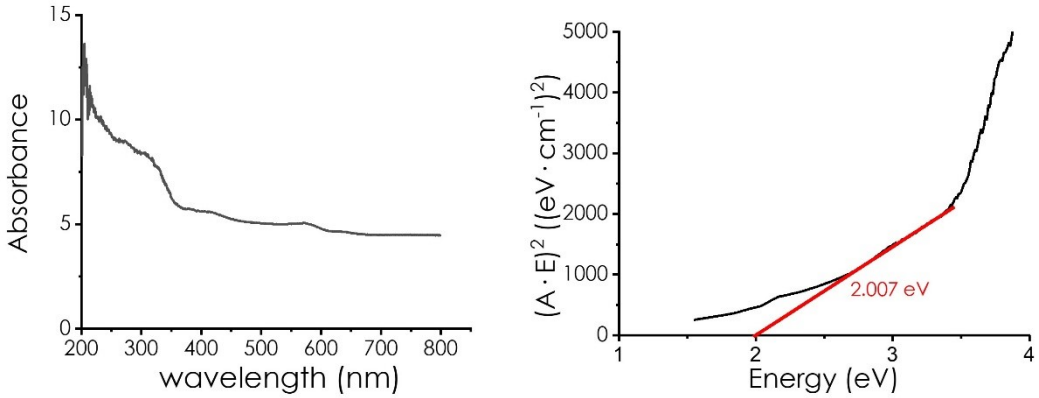


Figure S15. a) UV-Vis absorption spectrum of (N)C_a-2. b) Optical bandgap of (N)C_a-2 obtained from the Tauc plot of (N)C_a-2.

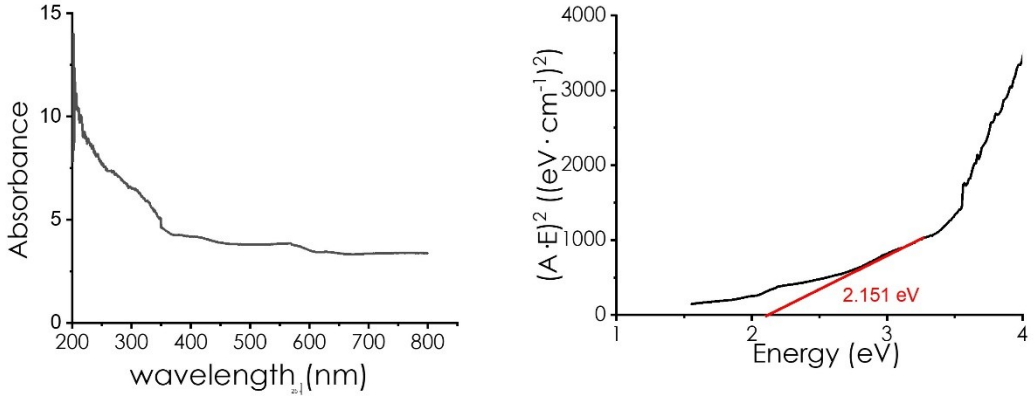


Figure S16. UV-Vis absorption spectrum of (N)C_{α}-3.

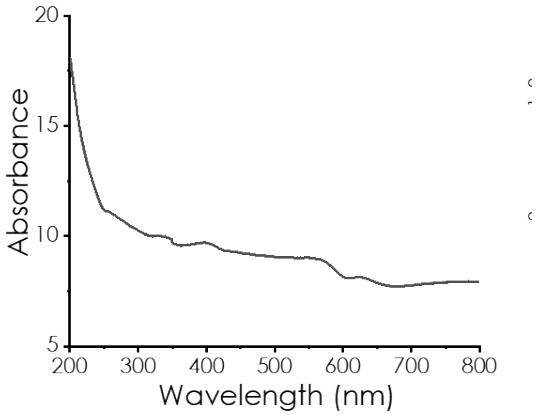


Figure S17. UV-Vis absorption spectrum of (N)C_{β}.

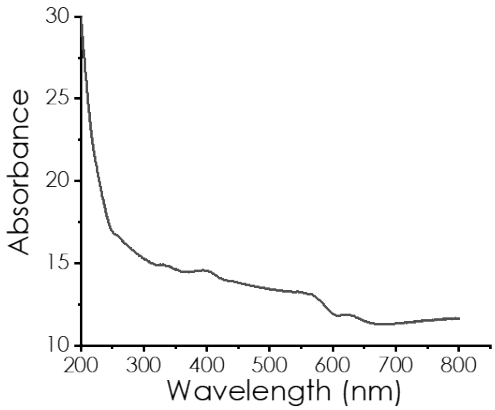


Figure S18. UV-Vis absorption spectrum of (N)C_{γ}.

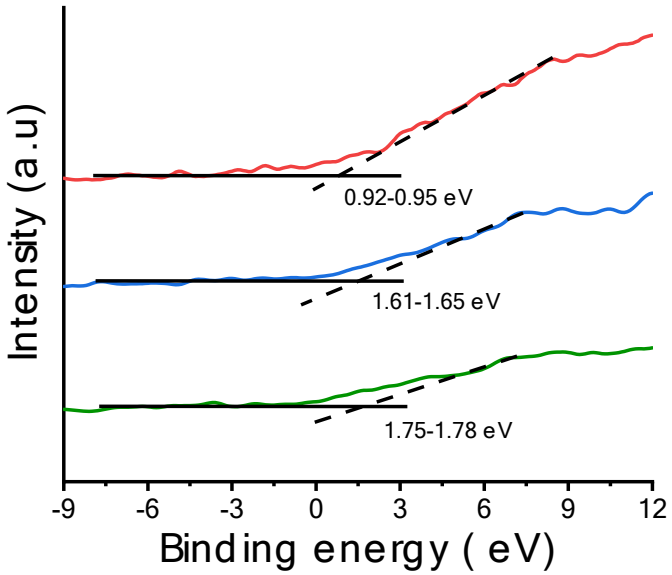


Figure S19. XPS Valance band spectra (N)C_α-1(red), (N)C_α-2 (blue) and (N)C_α-3 (green)

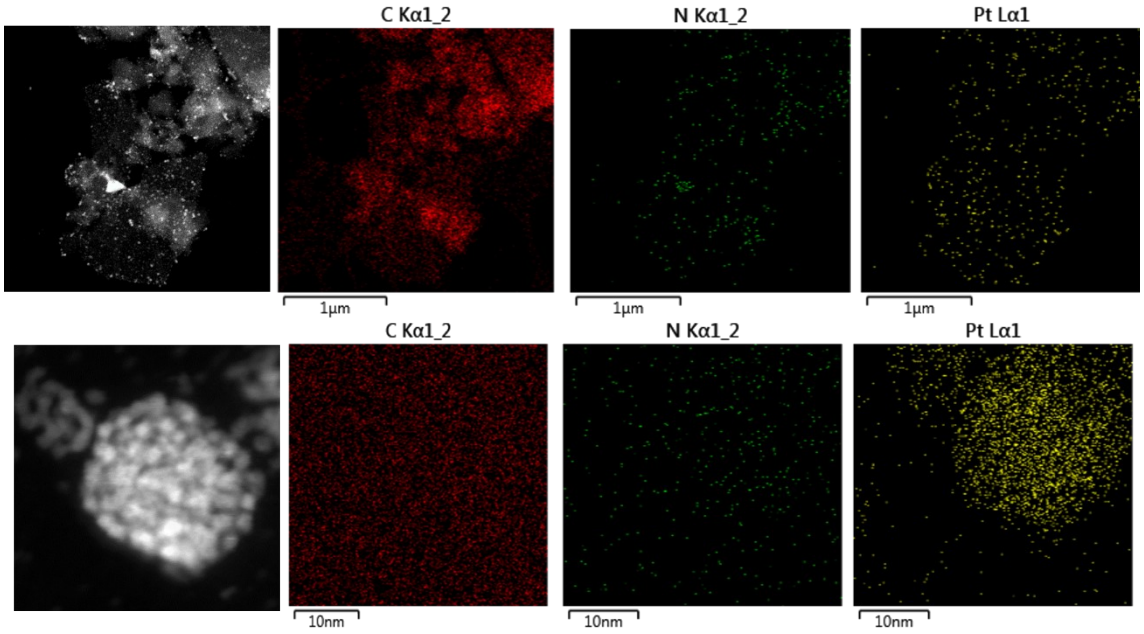


Figure S20. EDX analysis of (N)C_α-2 after irradiation in the presence of K_2PtCl_{6-}

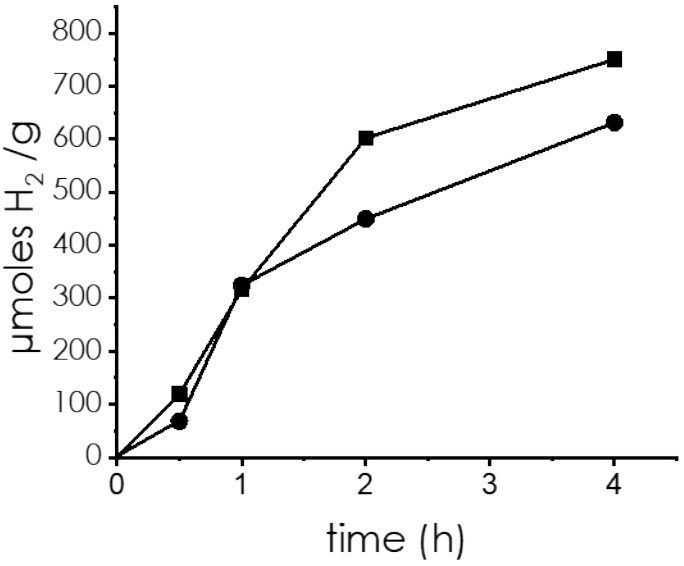


Figure S21. Temporal profiles of hydrogen evolution using as photocatalyst ●(N)C_α-2 and ■(N)C_α-2 containing the photodeposited Pt nanoparticles.

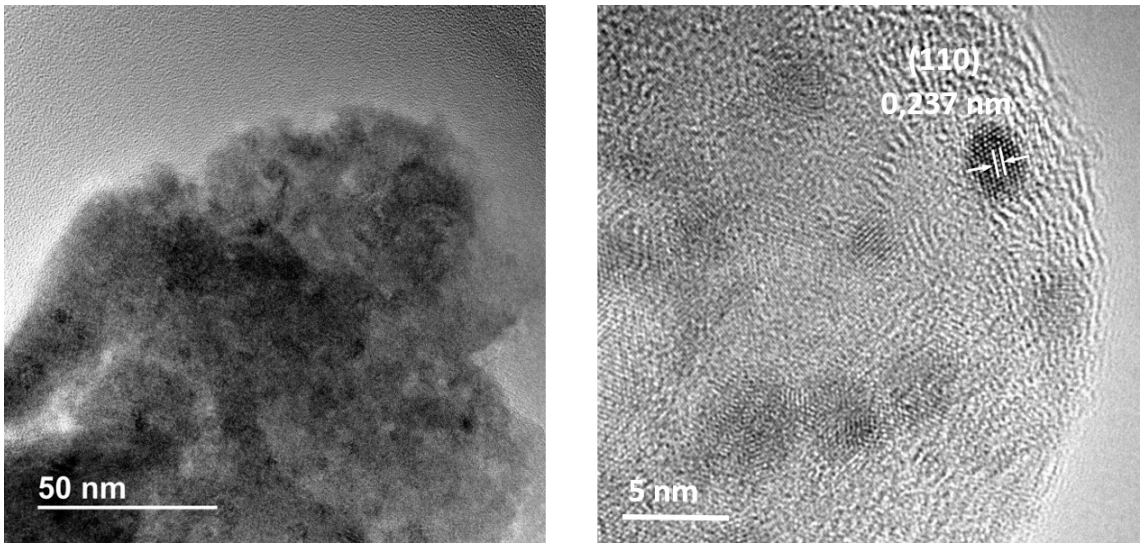
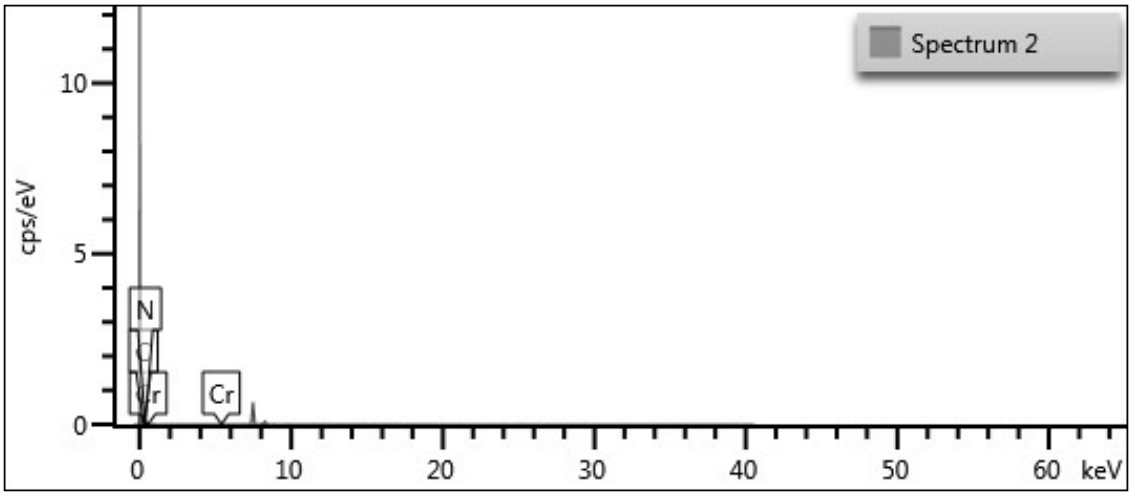


Figure S22. HRTEM images taken in transmission mode of (N)C_α-2 after irradiation in the presence of $CrCl_2$, where the formation of small Cr nanoparticles can be observed.



Element	Line Type	k Factor	k Factor type	Absorption Correction	Wt%
N	K series	3,515	Theoretical	1	49,42
Cr	K series	1,114	Theoretical	1	50,58
Total:					100

Figure S23. EDX analysis of (N)C_{α}-2 after irradiation in the presence of $CrCl_2$.

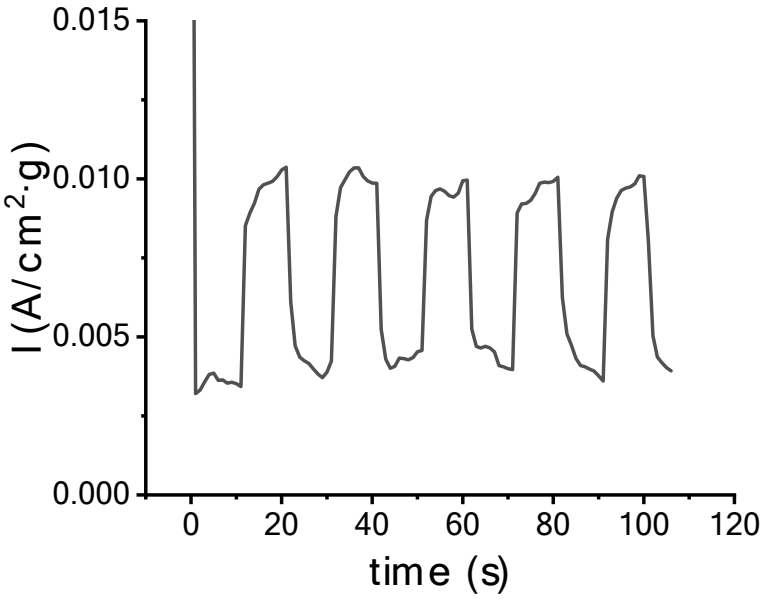


Figure S24. Photocurrent measurements of electrodes depositing (N)C_{α}-2 on FTO with UV-VIS light. Measurement conditions: 1 M aqueous KCl electrolyte, 500 W Xe lamp.

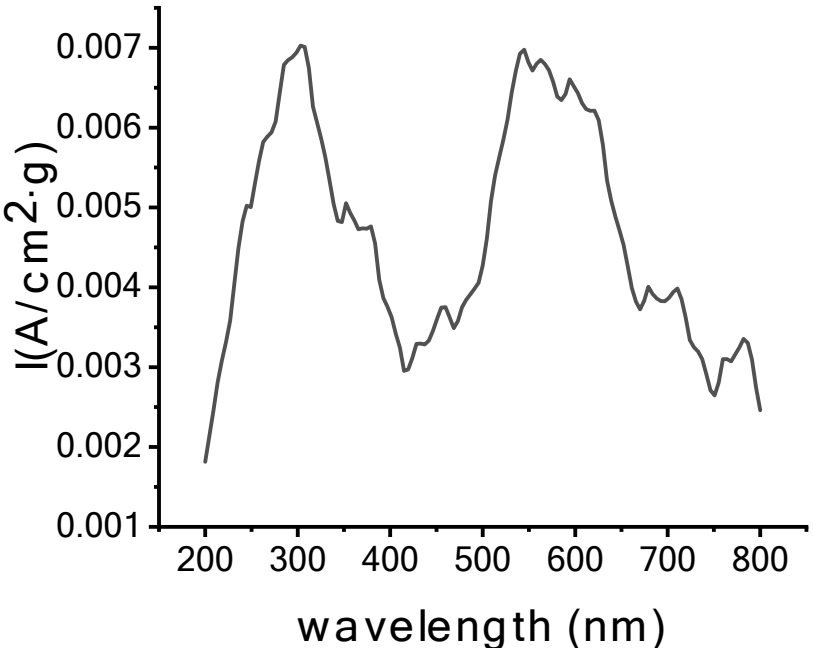


Figure S25. Photocurrent measurements of (N)C_α-2 on FTO electrode. Measurement conditions: 1 M aqueous KCl electrolyte, scan rate 5 nm/s, 500 W Xe lamp coupled with a Zolix Omni-λ-300D monochromator.

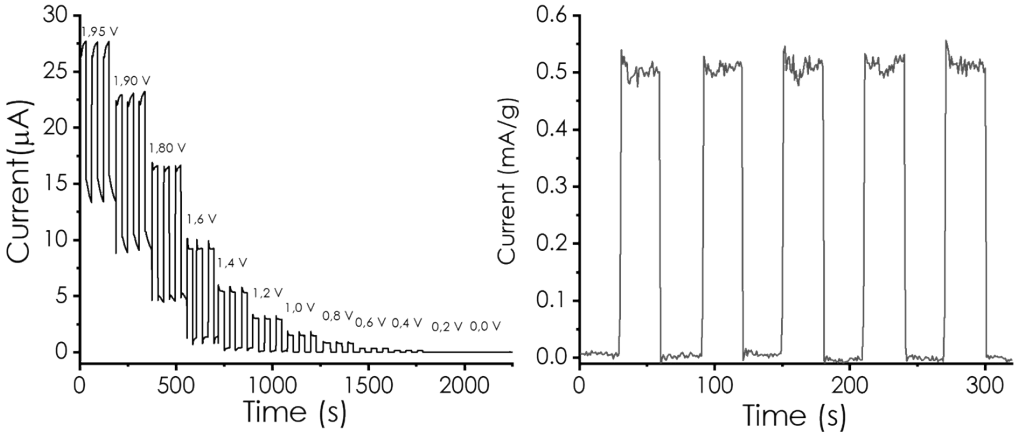


Figure S26. Chronoamperometric measurements of depositing (N)C_α-2 on FTO with UV-VIS light and photoresponse in open circuit.

Table S1. Comparison of the photocatalytic activity of (N)Ca-2 with other related materials reported in the literature.

Article	Catalyst	Conditions	Hydrogen
1	graphitic carbon nitride (GCN)	0,5 g L^{-1}, 1 wt% Pt, 10% TEOA, 300 W xenon-lamp (>420 nm)	2610 µmol h^{-1} g^{-1}
2	Nitrogen-Doped Functionalized Graphene Nanosheets (N-fGNS)	- g L^{-1}, 30% TEOA, 60 W xenon-lamp (>420 nm)	1380 µmol h^{-1} g^{-1}
3	nitrogen-doped graphene oxide-quantum dots (NGO-QDs)	6 g L^{-1}, visible light irradiation xenón-lamp 300 W (420 nm < λ < 800 nm)	0,3125 µmol h^{-1} g^{-1}
4	N-doped graphene is obtained by pyrolysis under an inert atmosphere of natural chitosan ((N)G)	0.057 g L^{-1},30 % metanol, 1000 W solar irradiation	3.20 µmol h^{-1} g^{-1}
5	3D nitrogen-doped graphene aerogel (3DNG)	0.188 g L^{-1}, 20 µL H_2PtCl_6, 10 % TEOA ,350 W xenon lamp	13.40 µmol h^{-1} g^{-1}
This article	N-doping of microporous graphitic carbons [(N)G_{CD}]	0,1 g/L, 20% metanol, 300 W xenon-lamp	1018 µmol h^{-1} g^{-1}

References

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4. C. Lavorato, A. Primo, R. Molinari and H. Garcia, *Chem. Eur. J*, 2014, **20**, 187-194.
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