Supporting Information for:

Monomers Sequence Design at Two Solvents Interface Enables the Synthesis of Highly Photoactive Carbon Nitride

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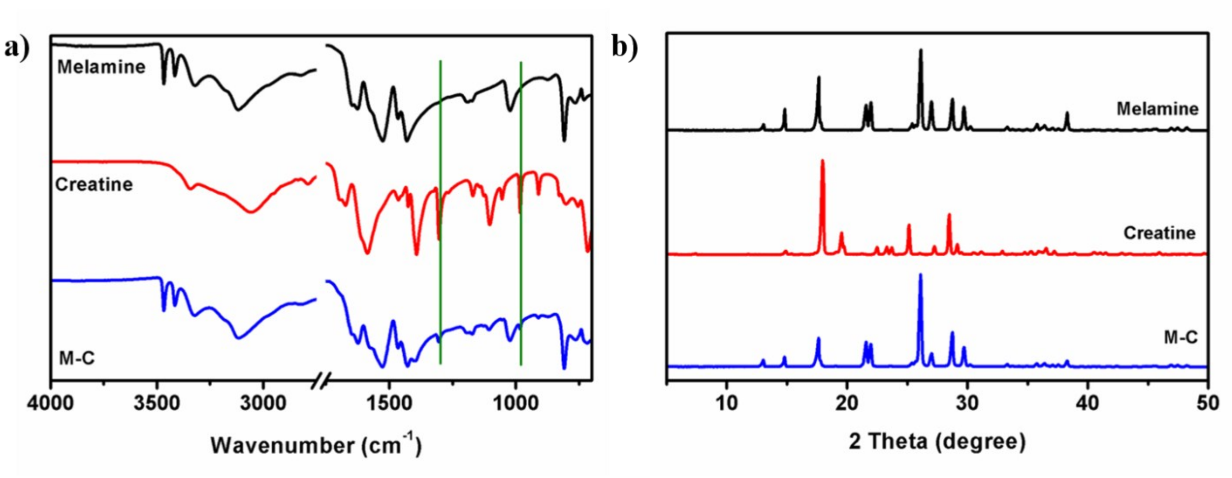


Figure S1. FTIR spectra (a), and XRD patterns of melamine, creatine and the supramolecular assembly of both.

FTIR spectra of the MC complex retains most of the features of melamine, as the C=N stretching vibrations, the N-H bending vibrations of the amine groups or the breathing mode of the triazine ring. Nevertheless, the vibrations from creatine corresponding to the tertiary amine at 1305 cm^{-1} and the O-H stretching at 980 cm^{-1} are present in the M-C, proving the interaction between both molecules. XRD spectra shows the slight suppression of the peaks at 17.5, 27.0 and 38.3 of melamine which correspond to the (110), (121) and (131) crystal planes.[1]

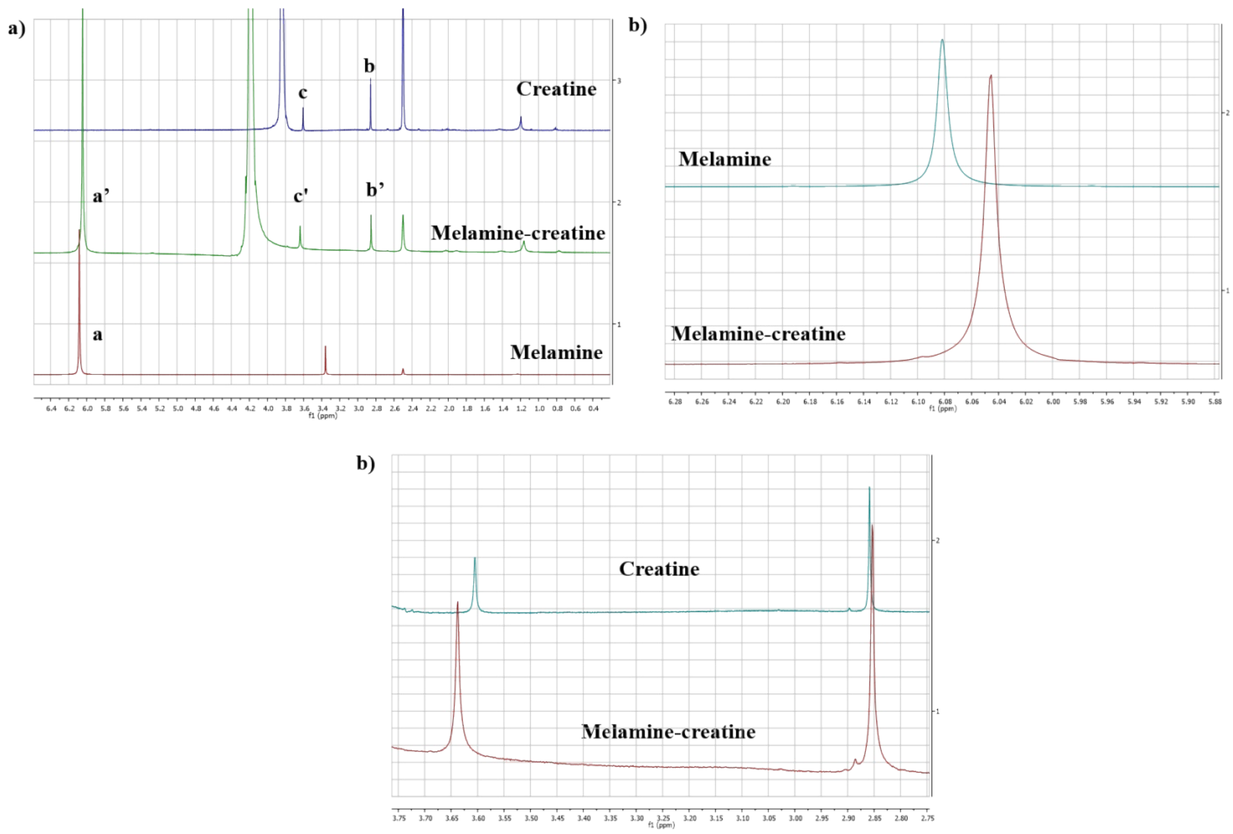


Figure S2. H^1-NMR spectrum of melamine, creatine and the supramolecular assembly of both (a), zoom of the spectrum of melamine and the supramolecular assembly (b), and zoom of the spectrum of creatine and the supramolecular assembly (c).

The structure of Melamine, creatine and the supramolecular assembly Melamine-Creatine was analyzed by ^1H NMR spectra. Figure S2 shows the corresponding labeled ^1H NMR spectrum. Melamine showed a broad singlet (a) at 6.08 ppm which corresponds to 6 protons of $–NH_2$ and creatine showed a singlet (b) at 2.86 ppm (3 H) which corresponds to 3 protons of the methyl group and a singlet (c) at 3.61 ppm (2 H) which is correspond to 2 protons of methylene group.

The ^1H NMR spectrum of the supramolecular assembly shows a clear shift in the signals of both compounds. Melamine $–NH_2$ protons signal slightly shifted up field and show the value (a') at 6.05 ppm (Figure S2a). Themethyl group peak that belongs to creatine (b)at 2.86 ppm (3 H) slightly changes the value up field (b’) at 2.85 ppm, and the methylene signal (c) at 3.61 ppm (2 H) shift to down field (c’) at 3.64 ppm (Figure S2b). The changes observed in the ^{1}H-NMRsuggest a feasible hydrogen bonding interaction between melamine and creatine to form supramolecular assemblies of melamine-creatine.

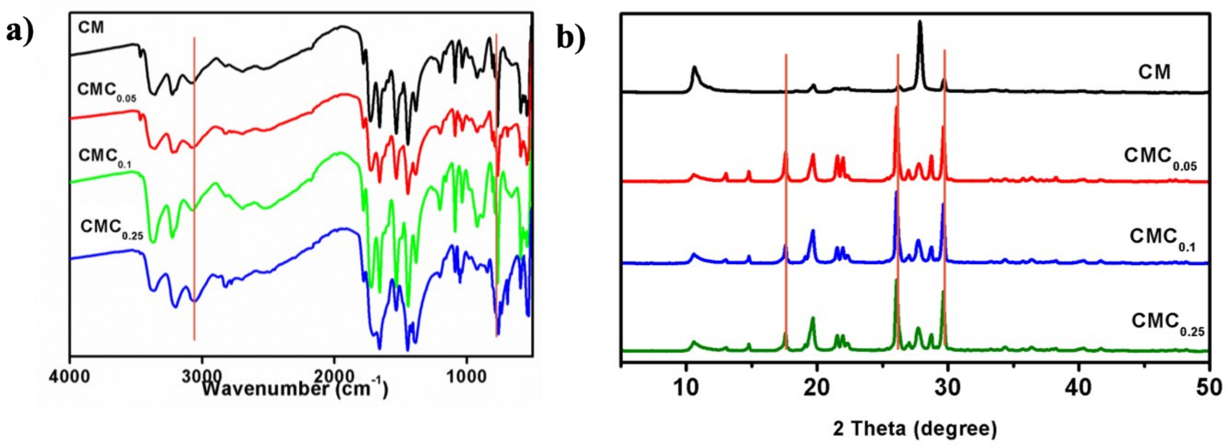


Figure S3. FTIR spectra (a) and XRD patterns (b) of CMC complexes.

Table S1. Elemental analysis of CMC complexes.

Sample name	N %	C %	C/N ratio	H %
CM	54.74	28.32	0.51	3.91
$CMC_{0.05}$	50.46	28.33	0.56	3.76
$CMC_{0.1}$	48.96	28.18	0.57	3.69
$CMC_{0.25}$	46.35	28.24	0.60	3.54

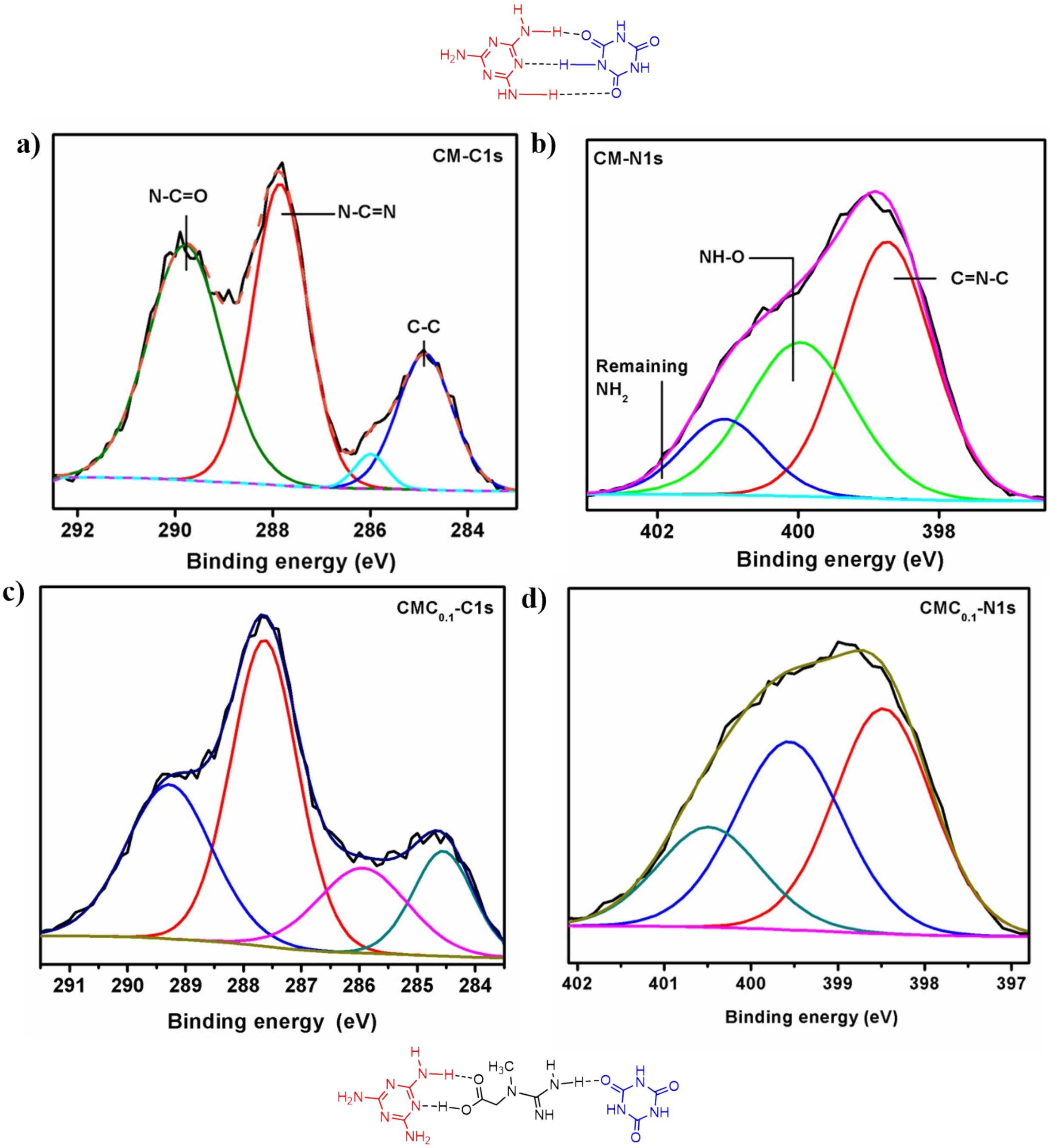


Figure S4. XPS measurements of CM (C1s (a) and N1s (b)) and $\mathrm{CMC}_{0.1}$ (c, d) with a scheme of the proposed structures.

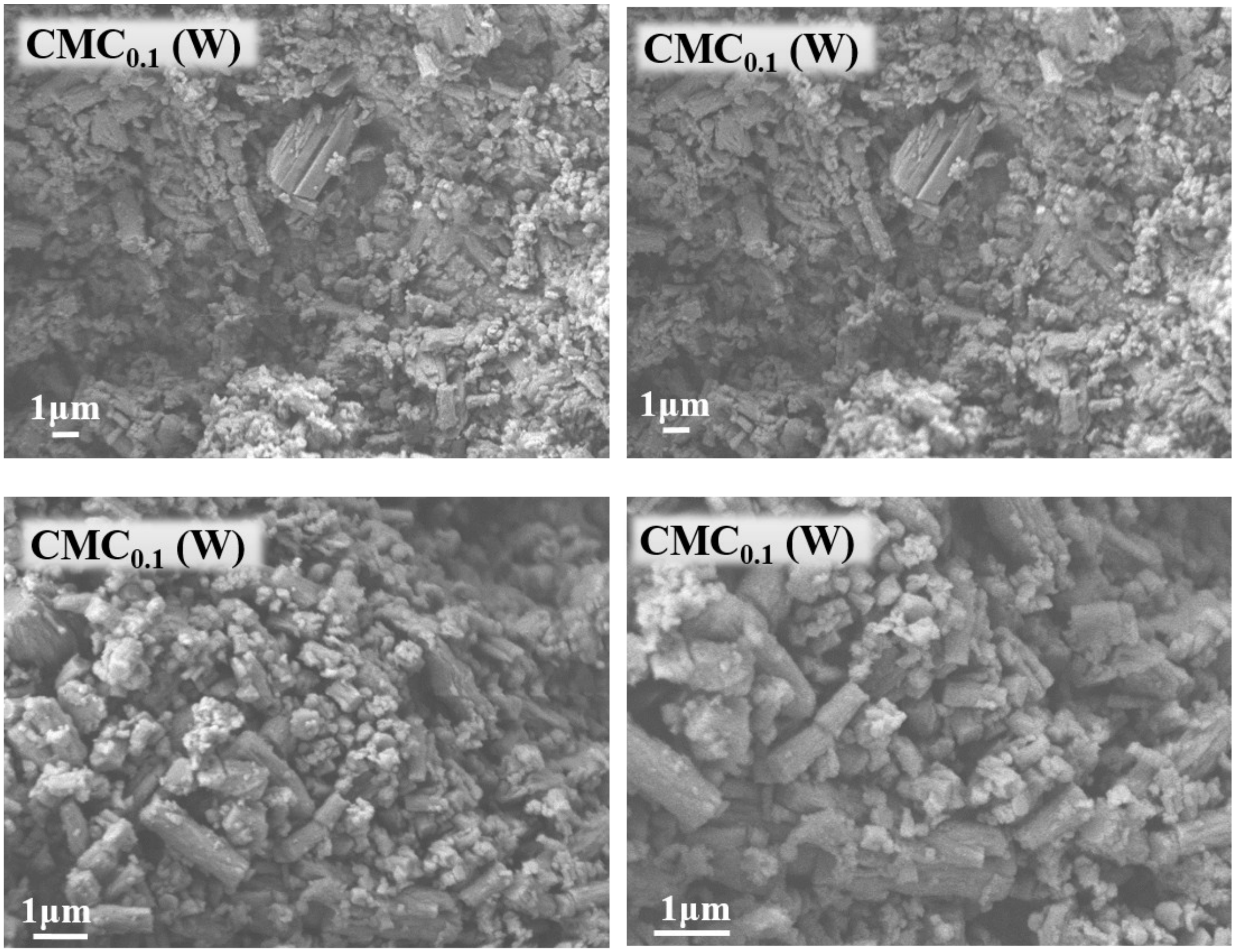
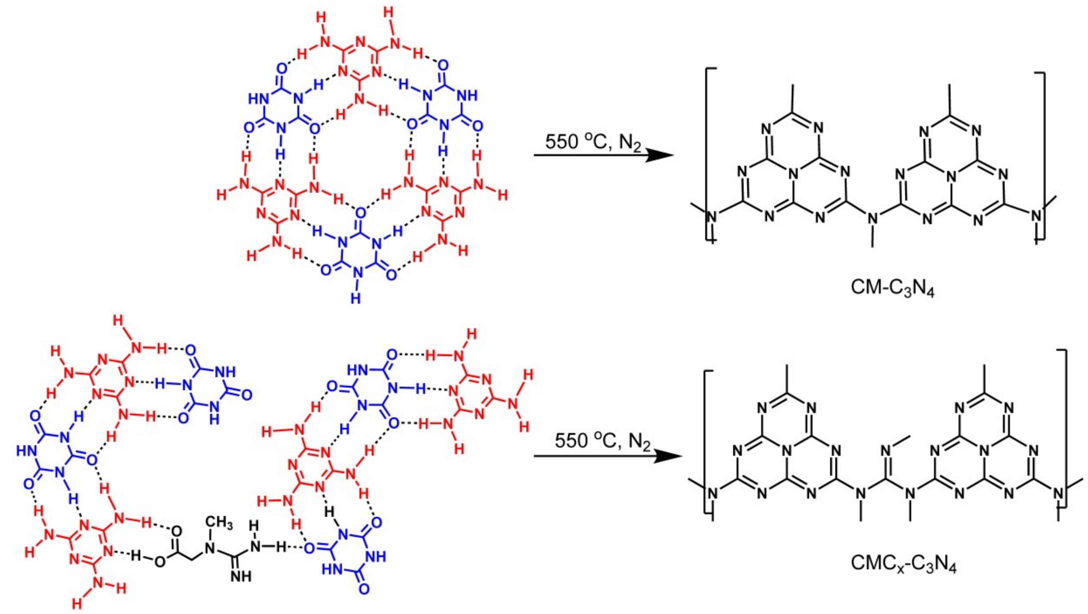


Figure S5. SEM images of the $CMC_{0.1}$ assembly synthetized in water only.



Scheme S1. Proposed structure of the modified carbon nitride materials prepared by using an aminoacid-grafted supramolecular assembly preorganized in a solvents mixture.

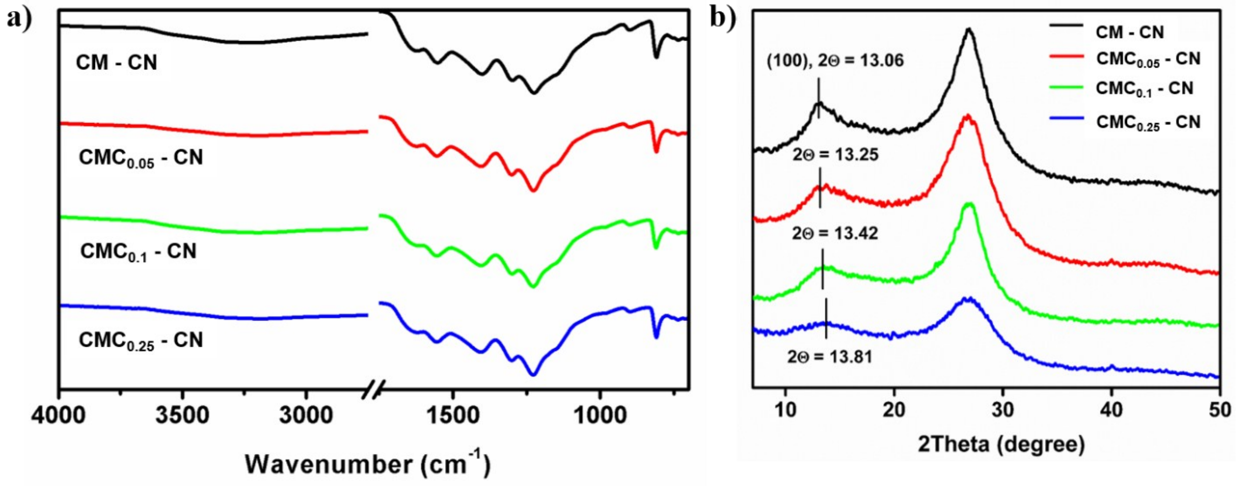


Figure S6. FTIR spectra (a) and XRD patterns (b) of CMC$_x$-CN materials.

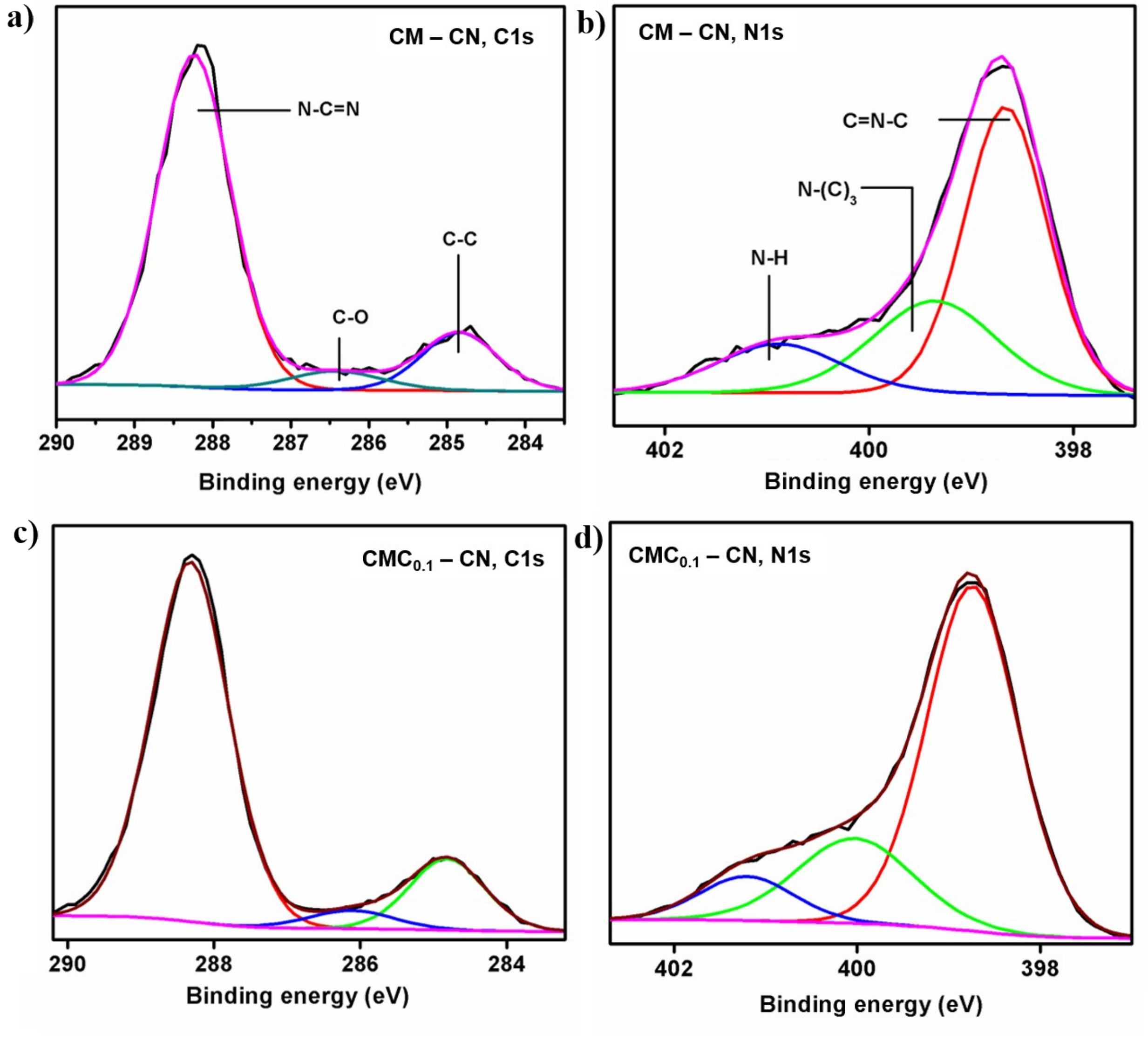


Figure S7. XPS measurements of CM-CN (a,b) and CMC$_{0.1}$-CN.

Both materials show the typical binding energies of graphitic carbon nitride with minor differences. CM-C_3N_4 and CMC$_{0.1}$-C_3N_4 C1s spectrum show three different chemical states, corresponding to adventitious C-C and C-O bonds, at 284.8 and 286.5 eV, respectively. N1s spectrum display also three different contributions at 398.7, 399.3 and 400.9 eV which belong to C=N-C of the heptazine rings, N-(C)$_3$ and remaining amino groups respectively.

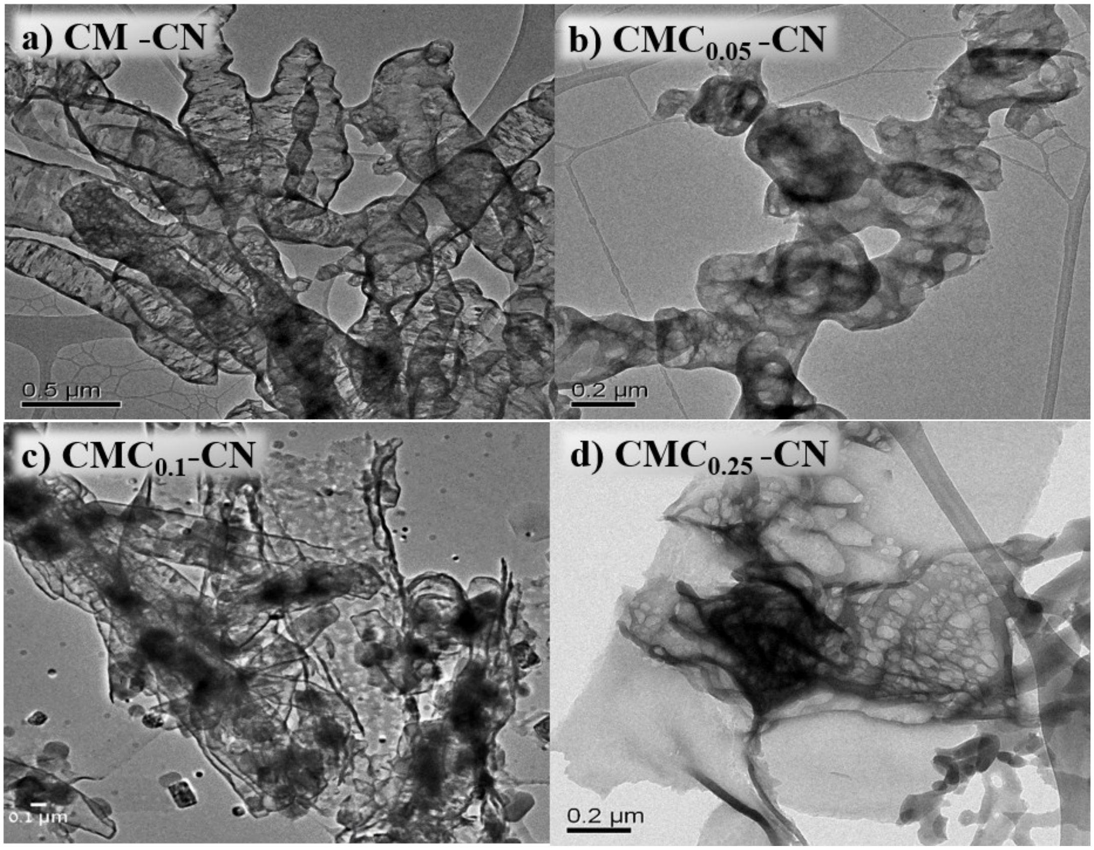


Figure S8. TEM images of CMC_x-CN materials.

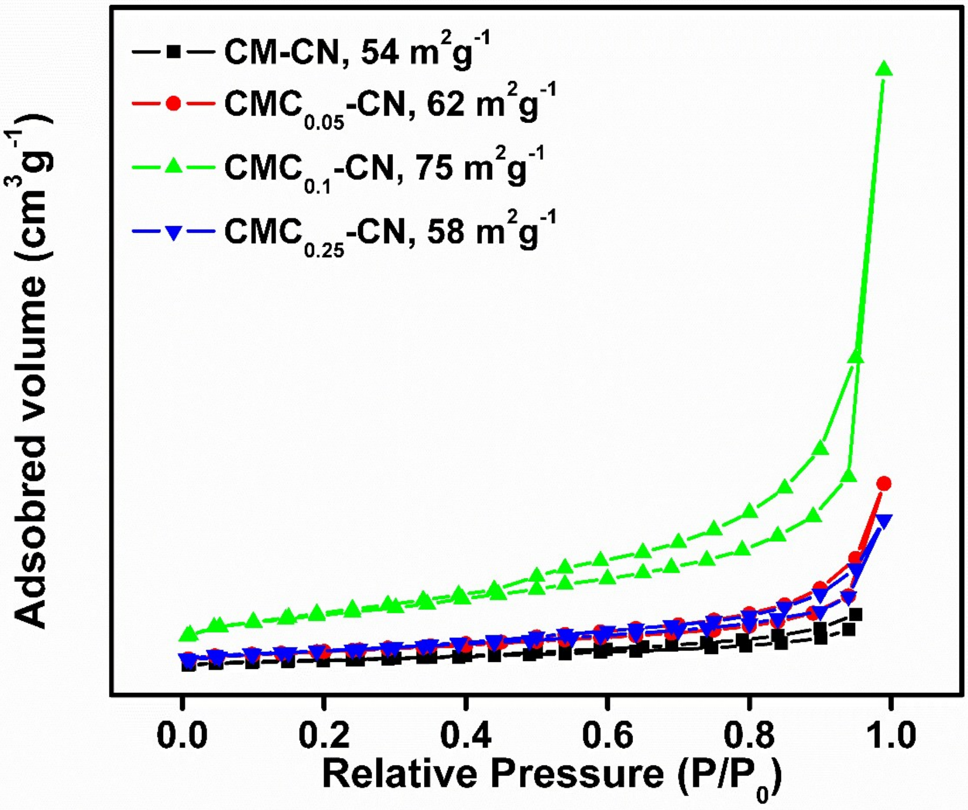


Figure S9. BET isotherms of CMC$_x$-CN materials.

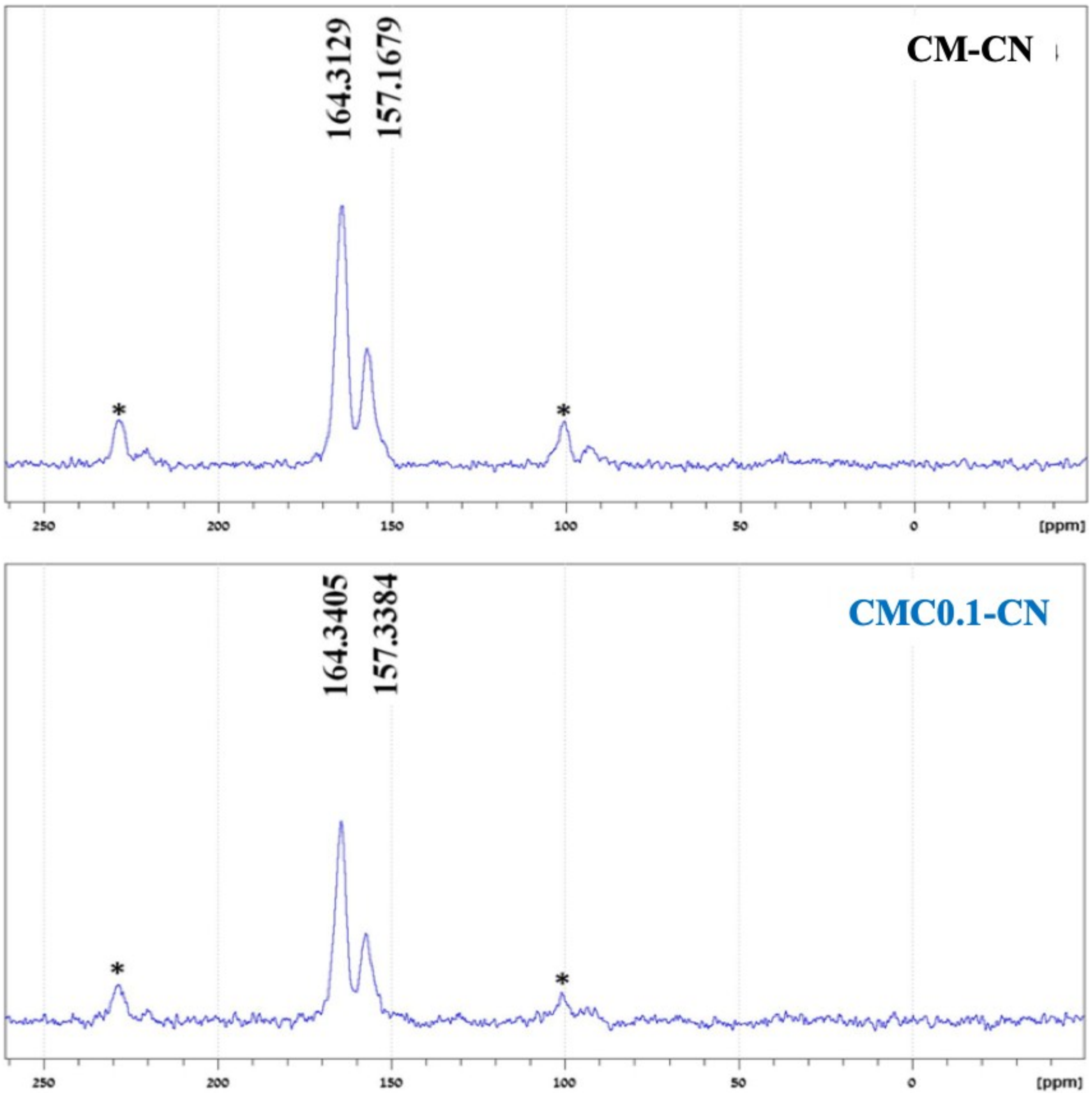
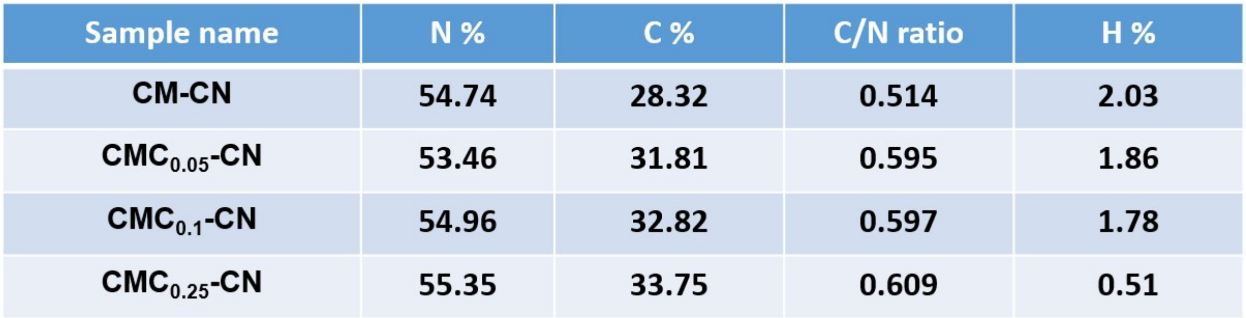


Figure S10. ^{13}C CP-MAS NMR spectra of carbon nitride powders (CM-CN and CMC$_{0.1}$-CN) * indicates the spinning side bands.

Table S2. Elemental analysis of CMC$_x$-CNmaterials.



Sample name	N %	C %	C/N ratio	H %
CM-CN	54.74	28.32	0.514	2.03
$CMC_{0.05}$-CN	53.46	31.81	0.595	1.86
$CMC_{0.1}$-CN	54.96	32.82	0.597	1.78
$CMC_{0.25}$-CN	55.35	33.75	0.609	0.51

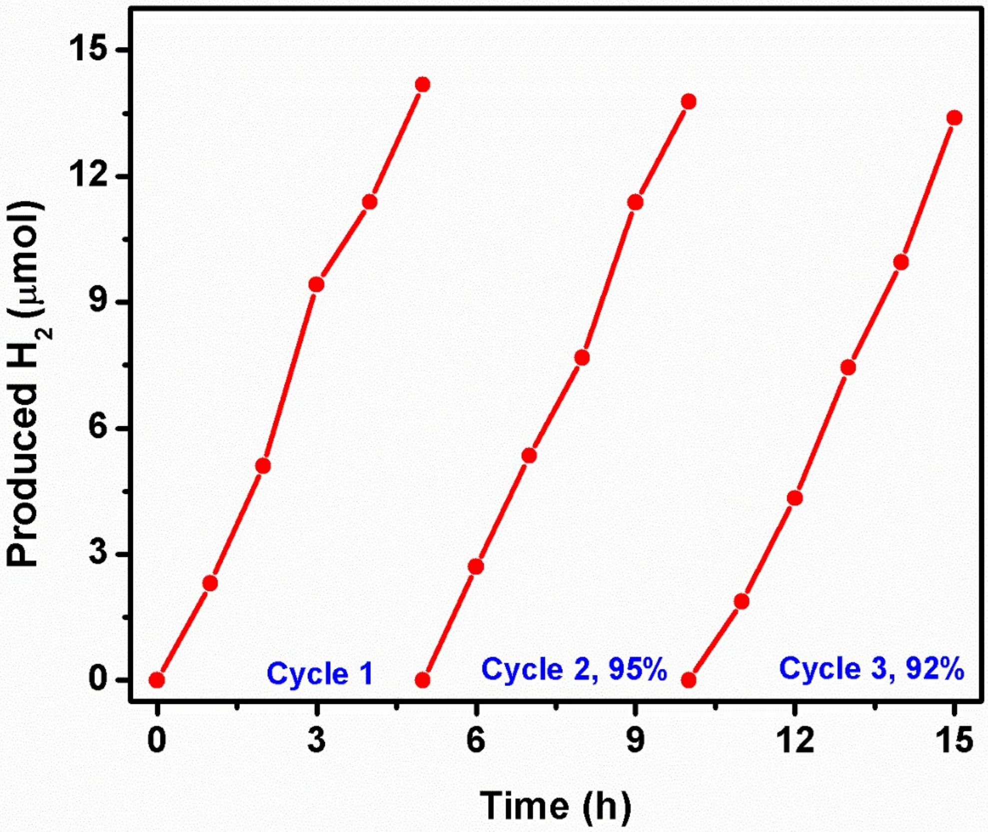


Figure S11. Hydrogen production of $CMC_{0.1}$-CN.

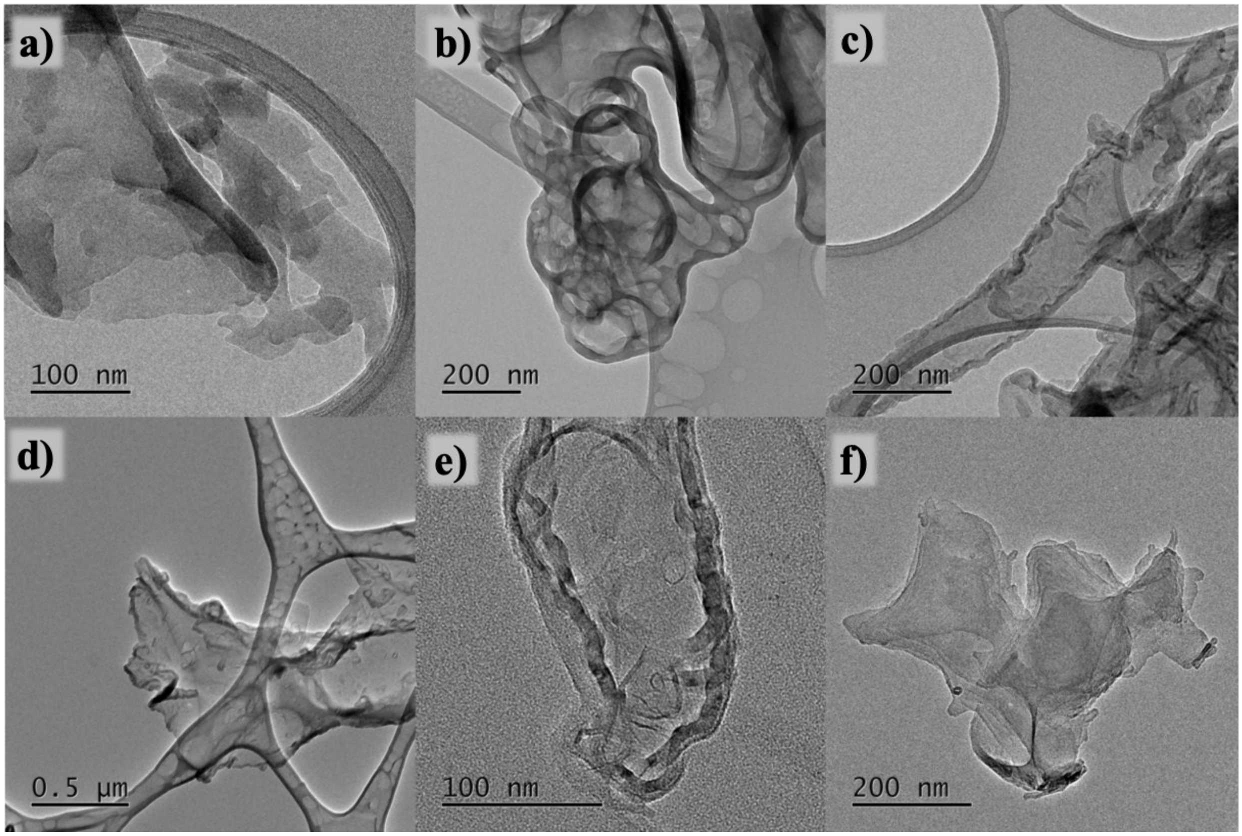


Figure S12. High resolution TEM images of CMC$_{0.1}$-CN before (a-c) and after (d-f) the stability test in the hydrogen evolution reaction. For this analysis, the samples were prepared by sonication-assisted exfoliation of a 0.5 mg mL^{-1} solution in isopropyl alcohol in a water bath for 2 h. The solutions were centrifuged at 4000 rpm for 10 min and the residual big aggregates were removed.

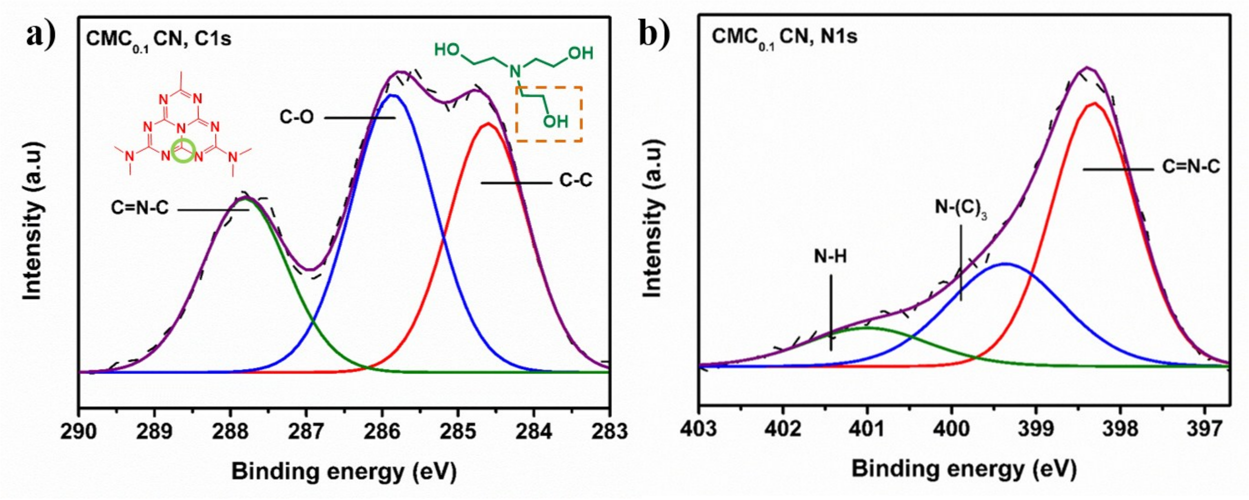


Figure S13. XPS analysis for C1s (a) and N1s (b) for $CMC_{0.1}$ CN after the photocatalytic hydrogen evolution measurement.

C1s spectra shows the typical CN contributions, with an increased weight percentage for the C-C, and C-O due to a feasible remaining of the triethanolamine utilized in the photocatalytic process as a hole scavenger.[2] Nevertheless, the C=N-C chemical bond is also present confirming the presence of the heptazine-based structure. N1s spectra shows the chemical bonds of CN materials, namely the C=N-C at 398.3 eV, tertiary amines at 399. 4 eV, and remaining amino groups at 401 eV.

REFERENCES

1. R. S. Bhosale, M. Al Kobaisi, S. V. Bhosale, S. Bhargava and S. V. Bhosale, *Sci. Rep.*, 2015, **5**, 14609.

2. B. Kumru, J. Barrio, J. Zhang, M. Antonietti, M. Shalom and B. V. K. J. Schmidt, *ACS Appl. Mater. Interfaces, 2019,* **11,** 9462-9469.