

## Defect-modulated photocatalytic response in 2D carbon nitride: a joint computational and experimental study.

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Graphitic carbon nitride (g-CN) is an interesting photoactive 2D material capable of catalyzing reactions such as water-splitting, CO<sub>2</sub> conversion and selective organic transformations and disinfections[1], with the advantage of being completely metal-free and presenting a narrower band-gap with respect to common metallic catalysts[2].

Recently some of us have demonstrated that the photo-catalytic response of g-CN can be modulated by convenient post-synthetic treatments[3]. More specifically, three correspondent post-synthetic forms, i.e. reduced (red. g-CN), amorphous (am. g-CN) and oxidized (ox. g-CN), were obtained, the amorphous (**am. g-CN**) showing the highest catalytic activity[3]. Through an experimental characterization, the enhanced photocatalytic efficiency of am. g-CN was hypothetically linked to the formation of a halogen-bond between an iodine atom of the perfluorobutyl iodide (C<sub>4</sub>F<sub>9</sub>-I) and the am. g-CN's surface.

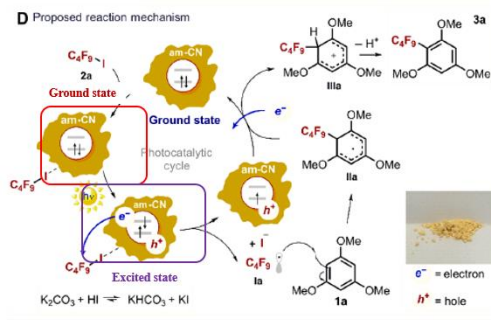
However, recent experimental investigations indicate that all the g-CN forms mentioned contain structural defects (nitrogen vacancies) with a radical carbon species, as confirmed by recent EPR measurements.

Herein, in order to provide a rationale to the photocatalytic response of different defective g-CN forms, we employed (Time-Dependent) Density Functional Theory calculations to study the ground-state and excited-state interactions between the C<sub>4</sub>F<sub>9</sub>-I substrate and the different g-CN forms. We find that the nitrogen vacancies in am. g-CN contain radical carbon/nitrogen units that not only interact strongly with C<sub>4</sub>F<sub>9</sub>-I but also generate mid-gap defect states within the electronic band-gap. These latter are directly responsible for the enhanced photo-induced charge transfer from defective g-CN's surface to C<sub>4</sub>F<sub>9</sub>-I, boosting the photo-catalytic response of am. g-CN's surface.

### References

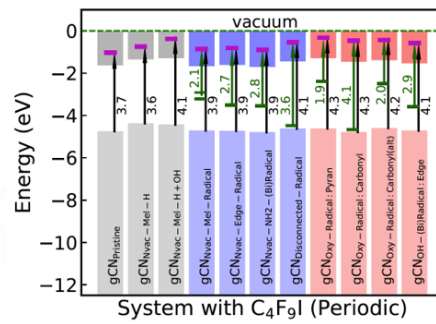
- [1] Jinliang Lin, et al., *ACS Sustainable Chem. Eng.* **2014**, 2, 3, 353–358.
- [2] Jiuqing Wen, et al., *Applied Surface Science* 391, (2017), 72–123.
- [3] Filippini et al., *Science Advances*, **2020**, Vol. 6, 46.

## Figures



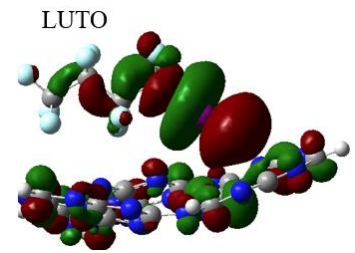
**Figure 1:**

The reaction mechanism proposed in [3]



**Figure 2:**

Electronic structure of the pristine (1<sup>st</sup> entry left) and the defective forms



**Figure 3:**

Electron density showing hybridization between the surface and the substrate