

# DFT MODELLING OF HYBRID 2D MATERIALS FOR LITHIUM PROTECTION IN LITHIUM-SULFUR BATTERIES

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## Introduction

In the field of lithium batteries there are great challenges to be met. Among them, one of the most important is the one that involves improving energy density in current devices due to the fact that it is very low to be implemented in applications that require high energy demand, such as electric vehicles [1]. In this way, “next generation batteries” can be found, like the lithium-sulphur ones and the lithium-air ones which noticeably improve the previously mentioned aspect [2,3]. However, these batteries in their design have metallic lithium as anode which is very reactive and involves a huge technological challenge for the mass production of these devices. Thus, different alternatives that concern the design of 2D materials which can be used as a protective layer of the anode are studied. The material of this previously mentioned layer must have the characteristics that allow the absorption and quick diffusion of the lithium ions to prevent the dendrites from growing.

## Objetives

We mostly analyse the efficacy of  $g\text{-C}_3\text{N}_4$  to be implemented as a protective layer of the lithium anode. For this, we carried out a characterization according to the descriptors based on the electronic nature while evaluating as well the effect of the doping with elements like P, O, S and B.

## Methodology

The modelling was performed with Quantum Espresso (QE) which implements the Density-Functional Theory (DFT) and uses periodic plane waves as a base (see Figure 1). We studied the thermodynamic adsorption of Lithium on different sites and its diffusion as well as the kinetic barriers for its diffusion through the nudged elastic band (NEB) method.

## Results and discussion

Figure 1a) illustrates the  $g\text{-C}_3\text{N}_4$  structure. The pristine and doped ( $X = \text{P}, \text{O}, \text{S}, \text{B}$ ) structures were optimized. Thereafter, we analyzed different possible sites for Li adsorption, based on the characterization of the electronic density, as shown in Figure 2. pDOS, Lowdin charges and the electrostatic potential all point to the different type of N atoms as the most likely interaction site for a positively charged atom as Li. Thus, we chose mainly four sites: hollow 1 ( $h_1$ ), hollow 2 ( $h_2$ ), on the aromatic ring (c) and on top of nitrogen 2 ( $\text{N}_2$ ), as it can be seen in Figure 3 a). Our calculations indicates that the binding energy or adsorption energy ( $E_{\text{ads}}$ ) of a Li atom on  $h_1$  and  $h_2$  is larger than in c and  $\text{N}_2$  (see Table I). The effect of doping in the interaction of Li on sites  $h_1/h_2$  is summarized in Table II.

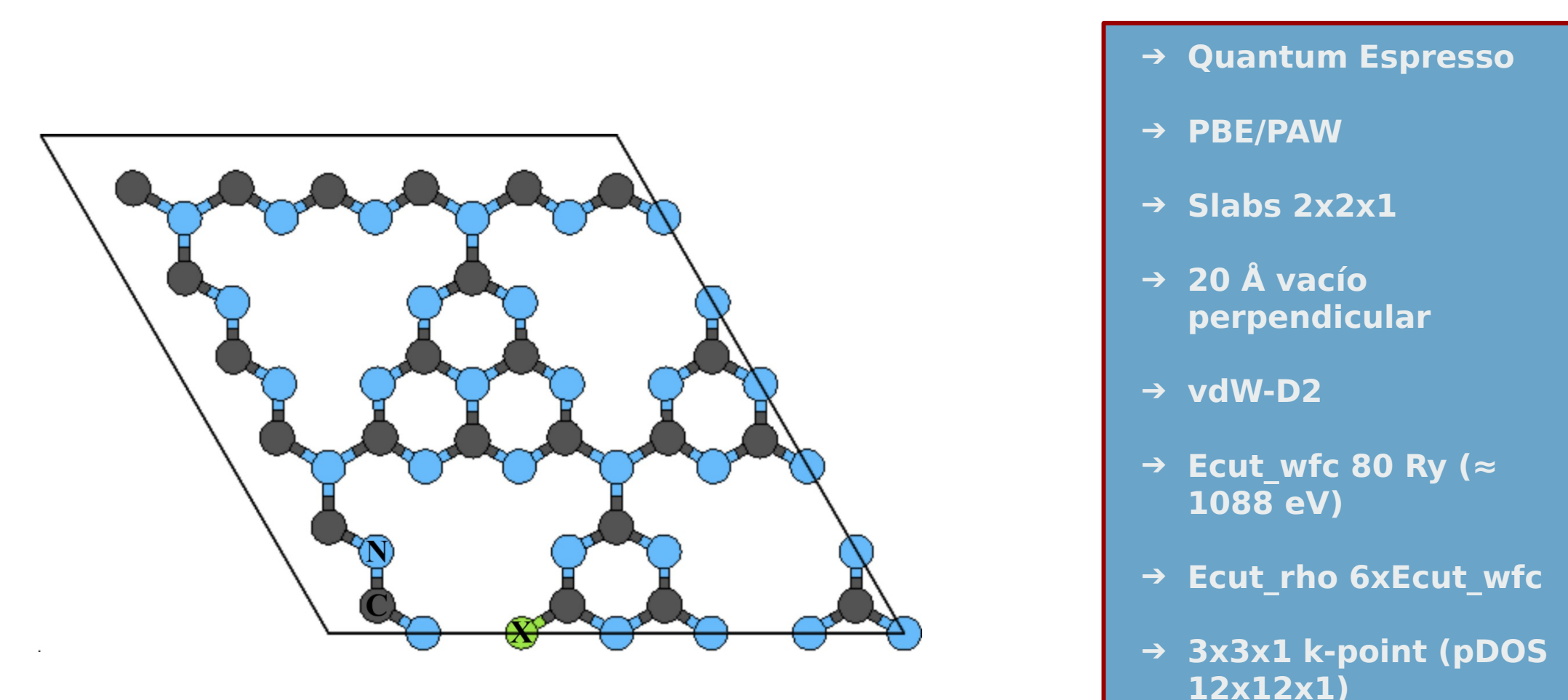
The largest adsorption energy value is obtained for  $X = \text{P}$ . As it can be seen from the atomic charge in Lithium ( $Q_{\text{Li}}$ ), this does not necessarily mean a larger charge transfer from Li to the surface. Some other bonding interaction must be at play. We are currently doing more detailed analysis in order to characterize this enhanced interaction.

## Conclusions y Perspectives

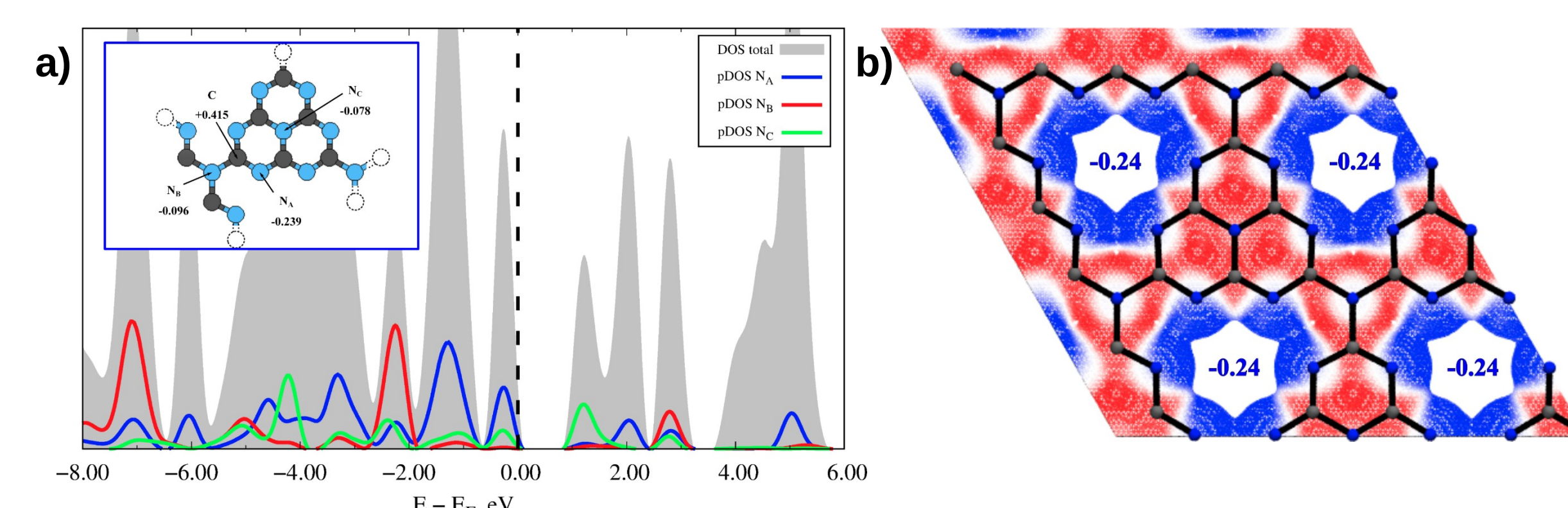
Based on what the obtained results, it can be suggested that doping on this type of surface might be favorable for the protection of the Li anode. The next step that is expected to be carried out is to determine the diffusion barrier on and through the surfaces.

## References

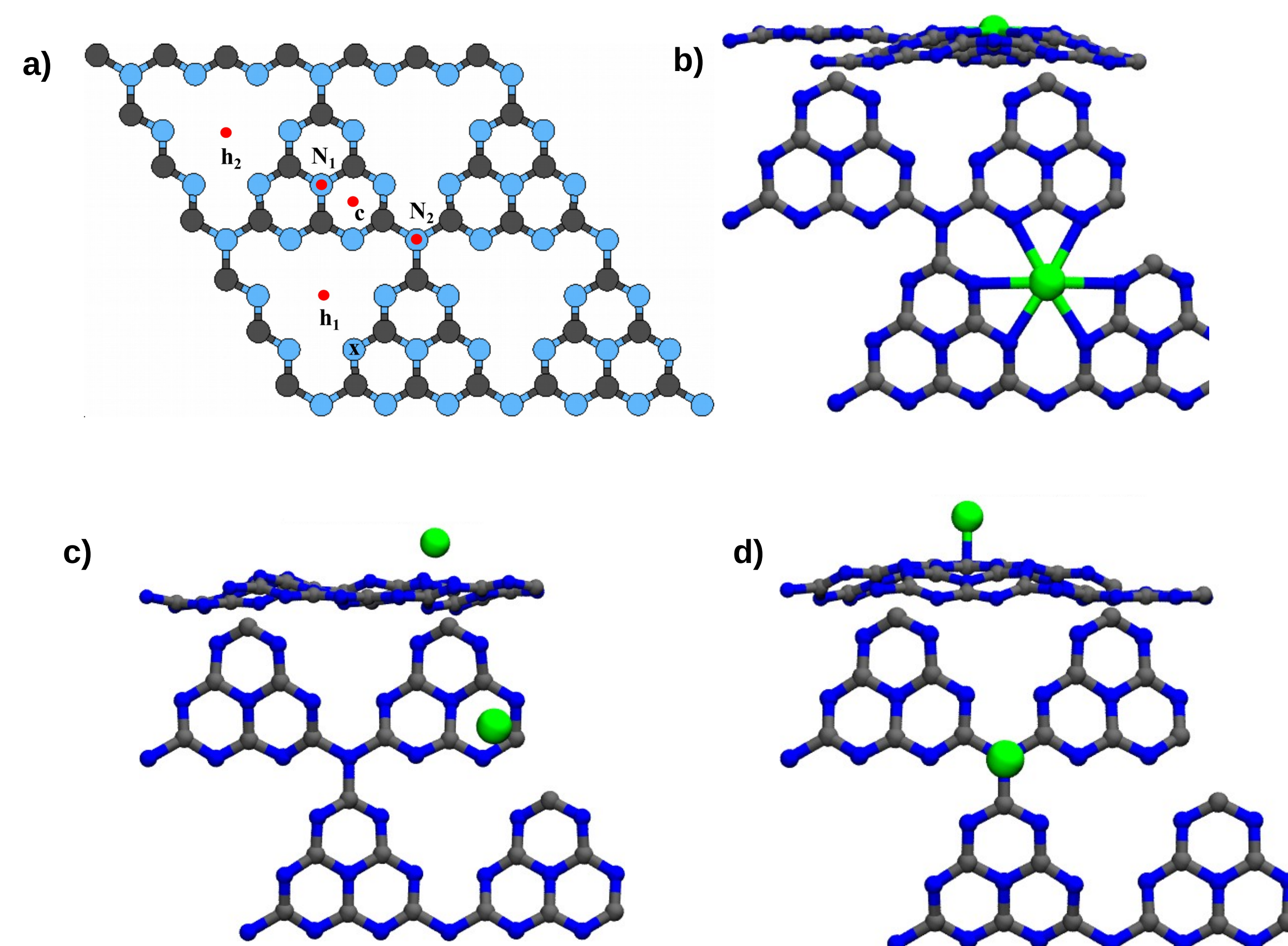
- 1) Zhang S. S., *ACS Appl. Energy Mater.*, **2018**, 1, 910-920.
- 2) Zhang X., Yang Y., Zhou Z., *Chem. Soc. Rev.*, **2020**, 49, 3040-3071
- 3) Zhang X., Yang Y., Zhou Z., *Chem. Soc. Rev.*, 49, 2040-3071 (2020)



**Figure 1.** a) Unit cell for the  $g\text{-C}_3\text{N}_4$  structure with  $X = \text{N}, \text{B}, \text{O}, \text{P}, \text{S}$ . b) Setup for the calculations



**Figure 2.** a) Density of states b) Isosurface of electronic density colored with the electrostatic potential in the scale from -0.01 Ry (blue) to +0.01 Ry (red).



**Figure 3.** a) Adsorption sites:  $h_1$  (hollow 1),  $h_2$  (hollow 2), c (on top to C),  $\text{N}_2$  (on top to  $\text{N}_2$ ) b) Li atom adsorption in  $h_1$  c) Li atom adsorption in c d) Li atom adsorption in  $\text{N}_2$

**Tables of adsorption energy**

i)		ii)	
Adsorption site	$E_{\text{ads}} / \text{eV}$	X / Site	$h_1 / \text{eV} (Q_{\text{Li}})$ $h_2 / \text{eV} (Q_{\text{Li}})$
$h_1 / h_2$	-3.78	N	-3.78 (+0.55)   -3.78 (+0.55)
$\text{N}_2$	-0.80	B	-3.64 (+0.42)   -4.37 (+0.52)
c	-1.50	O	-3.78 (+0.52)   -3.91 (+0.53)
		P	-4.75 (+0.37)   -4.93 (+0.53)
		S	-3.84 (+0.47)   -4.20 (+0.53)