DENSITY FUNCTIONAL THEORY AND EXPERIMENTAL STUDIES OF DOPED 2-D GRAPHITIC CARBON NITRIDE AND THEIR APPLICATIONS

ABSTRACT

Recently, enormous interest has been developed in graphitic carbon nitride (g-C_3N_4) compared to other inorganic semiconductors materials such as TiO_2, $SrTiO_3$, CdS, $BiVO_4$, TaON, and Ag_3PO_4, for a variety of applications, including photocatalysis, sensing, photovoltaics, etc. due to its superior performance and environmental friendliness. Although multifunctional features give g-C_3N_4 a promising future in various applications, its poor quantum efficiency prevents it from being used on a wide scale. Various strategies, such as heterojunction construction, defect control, coupling with carbonaceous materials, and doping, have been used to improve the quantum efficiency of g-C_3N_4. Significantly, the purposeful introduction of dopants is considered an important tool to enhance the structural, electronic, optical, and many other physical properties of g-C_3N_4. Electronic conductivity and electron mobility can be increased by replacing part of the carbon/nitrogen atoms or by interstitial doping in the crystalline structure of carbon nitrides. Doping also causes surface flaws in the carbon nitride structure, which is advantageous for efficient charge transfer. This work intends to elucidate the effect of element doping on the geometric, electronic, optical, magnetic, and catalytic properties of g-C_3N_4 using density functional theory (DFT) calculations. Single metal (Pt, Li, Na, Mn, Os, and Ir) or non-metal (P) doping and metal/non-metal co-doping are used in this study. After, the doping repositioning of frontier molecular orbitals (MOs) in the g-C_3N_4 monolayer is observed. The doped g-C_3N_4 monolayers reveal enhanced visible light response and more powerful optical absorption and conductivity than the pristine g-C_3N_4. After doping, there is a monotonous decrease in the work function values. Modification of non-linear optical (NLO) response due to Li and P co-doping into the g-C_3N_4 (Li/P-g-C_3N_4) monolayer has also been explored by DFT. The first hyper-polarizability (β) is enhanced from 1.84×10^3 au of pristine g-C_3N_4 to 5.85×10^4 au for Li/P-g-C_3N_4. Further, the consequence of Li and P functionalization on the g-C_3N_4 monolayer for hydrogen storage is investigated using DFT. The hydrogen storage capacity of 5.78 wt% is obtained after functionalizing Li and P into the g-C_3N_4. Next, the sensing performance of the pristine and Os, Ir, and Pt-embedded g-C_3N_4 for NO gas is studied using DFT. NO is found to be physisorbed on pristine g-C_3N_4 and chemisorbed on the Os, Ir, and Pt-embedded g-C_3N_4. We have also done experiments to validate some of our theoretical results. The degradation efficiency of methylene blue (MB) by Li/P-g-C_3N_4 as photocatalyst is found to be 83% which is significantly higher than the degradation efficiency of MB by pristine-g-C_3N_4 (49%) and single element doped, i.e., P-g-C_3N_4 (61.4%) and Li-g-C_3N_4 (69%) photocatalysts. The high degradation efficiency proves the potential of Li/P-g-C_3N_4 nanosheets to eradicate recalcitrant contaminants for environmental remediation concerns. Further, half-metallic ferromagnet nature is found in Mn/P-g-C_3N_4 with a magnetic moment and Curie temperature of 4.51 μ_B and ~ 800 K, respectively, which indicates that this material can be used in spintronic devices.

Keywords: Graphitic carbon nitride; element doping; catalysis; NLO response; hydrogen storage; gas sensing; dye degradation; spintronic devices