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Entitled

AB-INITIO INVESTIGATION OF 2D MATERIALS FOR GAS SENSING, ENERGY STORAGE AND SPINTRONIC APPLICATIONS

by

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Abstract

The field of two-dimensional (2D) materials has been extensively studied since their discovery in 2004, owing to their remarkable combination of properties. My thesis focuses on exploring novel 2D materials such as Graphene Nanoribbon (GNR), Holey carbon nitride C_2N, and MXenes for energy storage, gas sensing, and spintronic applications, utilizing state-of-the-art techniques that combine density-functional theory (DFT) and non-equilibrium Greens functions (NEGF) formalism; namely Vienna Ab-initio Simulation Package (VASP) and Atomistic Tool-kit (ATK) package. **Firstly**, on the side of gas sensing, the burning of fossil fuels raises the level of toxic gas and contributes to global warming, necessitating the development of highly sensitive gas sensors. To start with, the adsorption and gas-sensing properties of bilaterally edge doped (B/N) GNRs were investigated. The transport properties revealed that the bilateral B/N edge-doping of GNR yielded negative-differential resistance (NDR) IV-characteristics, due to the electron back-scattering which was beneficial for selective gas sensing applications. Therefore, both GNR: B/N were found to be good sensors for NO_2 and SO_3 respectively. After that, the catalytic activity of four magnetic transition metal "TM" elements (e.g., Mn, Fe, Co and Ni) embedded in C_2N pores, as single-atom catalysts (SAC), was tested towards detecting toxic oxidizing gases. The results of spin-polarized transport properties revealed that Ni- and Fe-embedded C_2N are the most efficient in detecting NO/ NO_2 and NO_2 molecules. **Secondly**, on the side of energy storage, since the fossil fuels reserves are depleting at an alarming rate, there is an urgent need for alternative forms of energy to meet the ever-growing demand for energy. Hydrogen is a popular form of clean energy. However, its storage and handling are challenging because of its explosive nature. The effect of magnetic moment on the hydrogen adsorption and gas-sensing properties in Mn-embedded in C_2N were investigated. Two distinct configurations of embedment were considered: (i) Single atom catalyst (SAC): 1Mn@C_2N; and (ii) Dimer atom Catalyst (DAC): Mn_2@C_2N. Based on the huge changes in electronic and magnetic properties and the low recovery time (i.e., $\tau \ll 1$ s, τ = 92 μs and 1.8 ms, respectively), we concluded that C_2N:Mn is an excellent candidate for (reusable) hydrogen magnetic gas sensor with high sensitivity and selectivity and rapid recovery time. Then, a comparative study of hydrogen storage capabilities on Metal-catalyst embedded (Ca versus Mn) C_2N is presented which demonstrated the stability of these metal structures embedded on the C_2N substrate. We proposed Ca@C_2N and Mn@C_2N for dual applications- hydrogen storage and a novel electrode for prospective metal-ion battery applications owing to its high irreversible uptake capacity 200/1100 $mAhg^{-1}$. **Thirdly**, on the side of data storage, spintronics is an emerging field for the next generation nanoelectronics devices to reduce their power consumption and to increase their memory and processing capabilities. Designing 2D-materials that exhibit half-metallic properties is important in spintronic devices that are used in low-power high-density logic circuits. We tested samples comprising of SAC and DAC of Mn embedded in a C_2N sample size 2×2 primitive cells as well as their combinations in neighboring large pores. Many other TM catalysts were screened and the results show the existence of half metallicity in just five cases: (a) C_2N:Mn (DAC, SAC–SAC, and SAC–DAC); (b) C_2N:Fe (DAC); and (c) C_2N:Ni (SAC–DAC). Our results further showed the origins of half-metallicity to be attributed to both FMC and synergetic interactions between the catalysts with the six mirror images, formed by the periodic-boundary conditions. **Lastly**, on the side of batteries, sodium-sulfur batteries show great potential for storing large amounts of energy due to their ability to undergo a double electron- redox process, as well as the plentiful abundance of sodium and sulfur resources. However, the shuttle effect caused by intermediate sodium polysulfides (Na_2S_n) limits their performance and lifespan. To address this issue, we proposed two functionalized MXenes $Hf_3C_2T_2$ and $Zr_3C_2T_2$ (T= F, O), as cathode additives to suppress the shuttle effect. We found that both $Hf_3C_2T_2$ and $Zr_3C_2T_2$ systems inhibit the shuttle effect by binding to Na_2S_n with a binding energy higher than the electrolyte solvents. They retained their metallicity during this process and the decomposition barrier for Na_2S_n on the O functionalized MXenes gets reduced which enhances the electrochemical process. Overall, our findings show that the tuning of 2D materials can lead to promising applications in various fields, including energy storage, gas sensing, and spintronics. The computational packages used in our study offer a powerful tool for investigating the properties of these materials and can provide insights for future research.

Keywords: 2D materials, Gas-sensing, Metal-ion batteries, Spintronics, Hydrogen storage, DFT, Metal-sulfur batteries.