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Computational design and functionalization of 2D materials and their heterostructures

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In the post-Graphene era, there has been a significant upsurge of interest on materials thinned down to its one or few atomic / molecular layer limit, and then exploring the new physics and applications emanating from these two-dimensional (2D) or quasi-2D nanostructures. Apart from Graphene and its analogues, there are studies on 2D alloy nanosheets exhibiting tunable band gap. The other emerging class of 2D material that is being explored exhaustively is the layered transition metal dichalcogenide family viz. MX_2 (M=TM, X=S, Se, Te). For example, there is an interesting manifestation of quantum size effect on the electronic behavior of layered VX_2 as a function of the number of layers. Many of these quasi-2D TMDC's, grown epitaxially on metallic or semiconducting substrates, result in lattice matched / mismatched heterostructures with different kinds of bonding ranging from weak Van der Waals bonding to relatively stronger ionic/covalent bonding. Physical and chemical properties of such overlayers often get modulated by the sub-surface layers of the corresponding substrates, leading to manifestation of new properties. In this talk, I shall discuss how density functional theory (DFT) based first principles simulation can be used in designing different classes of 2D materials and also to functionalize these for various applications in materials science and device physics [1-5]. Finally, I shall highlight the increasing relevance of combining machine learning and combinatorial techniques with DFT data base on 2D and quasi-2D materials.

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Carbon based nanostructures as metal-free catalysts: some case studies

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The ever growing demand and focus on energy and environmental issues have resulted in considerable attention being devoted to design and synthesis of cost-effective metal-free catalysts for low temperature fuel cells as well as for CO oxidation [1,2]. We discuss two novelcarbon based nanostructures that we have studied using state-of-the-art density functional theory (DFT) approach, viz. (a) [100] surface of T6-Carbon as oxygen reduction reaction (ORR) catalyst and (b) electron-doped 'holey' C_2N as CO oxidation catalyst.

(a) T6 carbon is a new and interesting allotrope of carbon that contains both sp^3 and sp^2 hybridized C atoms. This metallic form of carbon allotrope was predicted to be stable under ambient condition [3]. We have proposed, using DFT, a new metal-free catalyst viz. T6[100] surface [4], where the sp^2-C maintains the high metallicity needed to reduce ohmic loss and the sp^3–C helps in capturing the upcoming molecules, thereby making it a potential candidate for ORR. The top layered sp^3–C atoms of the surface are found to be more active towards ORR, as compared to that of sp^2–C atoms. As estimated from free energy profile, the over-potential is much lower when sp^3–C is considered as the active site and the final step i.e desorption of final OH^-ion is found to be the potential determining step.

(b) C_2N monolayer, a holey 2D (h2D) network nanostructure with a direct band gap of ~2.6 eV has been successfully synthesized [5] in the laboratory. Pristine C_2N monolayer is chemically inert, and hinders the adsorption of O_2 and CO molecule on it. Our DFT study shows that electron doped C_2N monolayer (O → N) acts as a metal-free catalyst for CO oxidation [6]. Oxygen doping in C_2N leads to increase in electron concentration of the system and introduces donor state below E_F (near conduction band). Thus the reactivity of O-doped C_2N ($2OC_2N$) monolayer gets significantly enhanced, thereby opening up the possibility of its usage as a catalyst. This active $2OC_2N$ surface adsorbs an incoming O_2 molecule via transfer of electron to its $2\pi^*$ orbital. Moreover elongation of O–O bond is observed, making it chemically active. Presence of this pre-adsorbed active O_2 greatly impedes the adsorption of another incoming CO, favoring Eley-Rideal (ER) mechanism for CO oxidation.

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