Transition-Metal Doped Polymeric Carbon Nitride for CO_2 Uptake

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Polymeric carbon nitride (PCN) is a two-dimensional, nitrogen-rich polymeric semiconductor composed of heptazine units, exhibiting high thermal stability, chemical robustness, and tunable electronic properties. These characteristics make PCN an attractive host for transition-metal dopants, as metal atoms can be strongly stabilized through metal–nitrogen coordination within the polymeric framework [1–4]. Recent experimental and theoretical studies have demonstrated that PCN can host both isolated and paired metal atoms through suitable coordination environments [1–4]. While TM-doped PCN systems have been explored for photocatalysis, cross-coupling, and CO_2 conversion reactions, systematic computational studies focusing on favourable CO_2 adsorption sites across broad combinations of dual-transition-metal (dual-TM)-doped PCN systems remain limited. Inspired by recent advances in geminal-atom catalysis [3], computational screening of dual-metal-doped g-C_3N_4 [4], and ML-assisted screening of dual-atom systems [5], this project aims to explore all possible pairwise combinations of selected first- and second-row TMs doped into PCN, including both homonuclear and heteronuclear combinations. By combining density functional theory (DFT) and machine learning (ML), I seek to identify stable dual-TM-doped PCN systems with favourable CO_2 adsorption characteristics.

To build the database, calculations were performed using plane-wave density functional theory with the Vienna Ab Initio Simulation Package (VASP). The projector augmented wave (PAW) method with the PBE functional within the generalized gradient approximation was employed. Spin-polarized calculations included dipole corrections, a 500 eV kinetic energy cutoff, and Γ-centered k-point grids (3×3×1) for surface models. Ionic relaxations were converged to forces below 0.05 eV $Å^{-1}$ and electronic self-consistency to 10^{-6} eV. CO_2 adsorption will be systematically evaluated at different sites on each dual-TM-doped PCN structure. The structural and energetic descriptors results will then be used to develop ML models capable of identifying structure–property relationships and ranking favourable CO_2 adsorption environments. This combined DFT–ML workflow is intended to accelerate the screening of different metal-pair and adsorption-site combinations and guide the identification of promising systems for more detailed studies of CO_2 adsorption.

The project aims to establish a transferable computational framework for the design and screening of PCN-based dual-TM-doped systems, with broader relevance to sustainable chemical manufacturing and carbon-utilization technologies. The resulting framework may also provide a foundation for future collaborative studies combining atomistic simulations and ML approaches for materials screening on two-dimensional supports.

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