First-Principles Study of Graphene/Blue Phosphorus/Graphitic-ZnO van der Waals Heterostructures: Optoelectronic Enhancement and Mn Doping Effects

Two-dimensional van der Waals (vdW) heterostructures exhibit unique electronic and optical properties, making them strong candidates for next-generation optoelectronic devices. Our previous work demonstrated that adding graphene (G) into a black phosphorus/graphitic ZnO (g-ZnO) bilayer enhances thermal stability and carrier transport through orbital hybridization, interlayer coupling, and strain effects, increasing the solar cell efficiency from 3.5% to 14.7%. In this study, density functional theory (DFT) calculations using the GGA-PBE functional implemented in CASTEP are extended by replacing black phosphorus with blue phosphorus (Blue-P), which possesses a similar hexagonal structure to G and g-ZnO. The new design effectively reduces lattice mismatch and improves interface stability. Furthermore, single-atom Mn doping is introduced into g-ZnO to modulate its electronic and optical behavior. Electronic structure analysis reveals that both G/Blue-P/g-ZnO and G/Blue-P/Mn–g-ZnO show type-II band alignment with indirect bandgaps. Optical properties show that G/Blue-P/g-ZnO achieves significantly enhanced absorption across the visible spectrum, increasing the solar cell efficiency to 26.6%, whereas Mn doping decreases it to 7.6% due to modified band structure of the heterostructure. The result demonstrates the tunability of 2D vdW heterostructures and provide valuable insight into single-atom doping strategies for designing high-performance optoelectronic materials.