

Hybrid Functional Study on Electronic and Optical Properties of the Dopants in Anatase TiO₂

W. A. Chapa Pamodani Wanniarachchi,* Thevakaran Arunasalam, Punniamoorthy Ravirajan, Dhayalan Velauthapillai,* and Ponniah Vajeeston



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ABSTRACT: TiO₂ was known as a golden heterogeneous photocatalyst due to its chemical stability, low cost, nontoxicity, and strong oxidizing power. However, anatase TiO₂ predominantly absorbs the photon energy in the ultraviolet region ($\lambda < 387.5$ nm); therefore, to increase the utilization of sunlight, the approach of doping of metals and nonmetals into pure TiO₂ is implemented. Here we incorporate the dopants of Zr, Si, V, W, Ge, Cr, Sn, Mo, and Pb into the TiO₂ lattice and study the optoelectronic properties, including the formation energies and the electron charge distributions, using the Vienna ab initio Simulation Package (VASP) from the hybrid functional of Heyd, Scuseria, and Erhzerhof (HSE06). We observed that V-, Mo-, and Cr-doped systems introduce shallow impurity states within the band gap, and those states influence the shift of the absorbance spectra to visible light by enhancing the photocatalytic efficiency. W-doped anatase TiO₂ structure reduces the band gap of the pure anatase TiO₂ by 0.7 eV. Notably, this reduction occurs without the introduction of any impurity states between the band edges. Additionally, the absorption edge of the solar spectrum shifts toward lower photon energy from 3.5 to 3.1 eV. From Bader charge analysis, we observed that mainly the charge transfer occurred from the dopants and charge accumulation happened around nearby oxygen atoms. The ferromagnetism was observed in V-, Cr-, Mo-, and W-doped anatase TiO₂ structures due to the charge imbalance of the spin-up and spin-down states.

