Chapter 3
Strategic Heteroatom Doping for Electronic Tuning and Redox Optimization in Functional Materials

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ABSTRACT

The increasing need to use high-performance materials in energy storage, energy catalysis, electronics and sensing has heightened efforts to seek ways of precisely controlling the electronic and chemical characteristics of these materials. The deliberate introduction of foreign atoms into a bulk lattice, heteroatom doping, has proven to be a potent and scalable method of controlling the band structure, charge dynamics, and reactivity at the surface. This chapter will discuss strategic boron (B), nitrogen (N), and phosphorus (P) doping in functional materials with a particular focus on their specific contributions to the redox behavior and electronic structure. B represents the introduction of electron-deficient sites to increase the oxidation activity, N increases the electron density to promote conductivity and

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reduce selectivity, and P brings about lattice distortion, creating more active sites and ion storage capacity. B-N and N-P combinations exhibit synergies whose effects are greater than those of single dopants.

1. INTRODUCTION

The search of high-performance functional materials has been more vigorous over the last decades, feverishly preoccupied with the pressing need to transform energy effectively, store energy sustainably, and develop catalytic architectures of the future to clean up the environment. The ability to manage and regulate the inherent nature of materials at their atomic and electronic level is at the core of this development. Doping can modify the local electronic environment by replacing or adding atoms to a host lattice to allow the tailoring of local conductivity, catalytic activity and stableness precisely. The doping of non-metallic heteroatoms (boron, N, and phosphorus) in particular has been of great interest (Shinde et al., 2025). Their relatively low atomic sizes, variety of valences state, and different electronegativities enable them to introduce controlled perturbations of the electronic configuration of the host material. Boron has its effect on the concentration of holes, with its deficiency of electrons, whereas nitrogen, more electronegative, has an effect on the concentration of electrons in active locations and better electron transport, and phosphorus, which has a larger atomic radius and lower electronegativity than nitrogen can expand the lattice, lowering the energy of bandgaps, and increasing the overall conductivity. The strategic placement of these heteroatoms does not simply affect the bulk electronic structure it also affects surface chemistry and interfacial phenomena which are important in redox reactions in photocatalysis, electrocatalysis, and energy storage. An example is that nitrogen doping of graphitic carbon materials can generate high-density active sites to undergo oxygen reduction reactions and boron doping of metal oxides can enhance charge separation after photogeneration during solar-driven water splitting. Phosphorus doping has been demonstrated to stabilize transition metal catalysts, to inhibit dissolution, and to enhance the life of the cycle in an electrochemical energy device (E. Zhang et al., 2021). More recent developments in synthetic methods, such as chemical vapor deposition and hydrothermal methods, as well as atomic layer deposition and plasma-assisted doping, have allowed control of both dopants concentration, distribution, and bondages to be controlled with accuracy. Such techniques as X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR) and state-of-the-art synchrotron techniques have given new insight on a hitherto unseen level of perception of the coordination and electronic states induced by doping (Song et al., 2022). These