Abstract

The present work focuses on mechanistic insights into the catalytic performance of functional graphitic carbon nitride (gCN) based heterojunction photocatalysts for the degradative removal of several emerging organic contaminants from aqueous medium.

The functionalized gCN was synthesized using solid state calcination and thermal exfoliation method. The subsequent growth of mixed metal oxides and/or semiconductors were achieved through solvothermal/hydrothermal techniques. Functional gCN was prepared through incorporating N-defects and Co, Ce oxide doping into its matrix, and various binary and ternary composites, including $CoFe_2O_4$/gCN, gCN/$CuFe_2O_4$/MoS_2, $ZnFe_2O_4$/gCN/Bi_2S_3, doped gCN/Bi_2S_3, and Bi_2MoO_6/doped gCN. Using peroxymonosulfate (PMS) activation and UV/Vis irradiation, these composite catalysts were employed for the degradative mineralization of reactive dyes (RDs), 2,4,6-trichlorophenol (TCP), ciprofloxacin (CIP), amoxicillin (AMOX), and tetracycline (TC). Within 20-60 minutes of UV/Vis light exposure, 0.1-0.4 g/L of various catalysts and 0.5-1.75 g/L PMS dose combinations could achieve 98-99.9% degradation of organic pollutants with ≥73% mineralization efficiency. The impacts of different operational parameters on degradation efficiency were investigated. By radical scavenging and EPR analysis, the distinct radical species generated in the medium were detected. Based on different in-depth characterization studies, the comprehensive mechanism of PMS activation, radical generation, along with the identification of different surface bound redox cycles, i.e., $Co^{2+}/Co^{3+}\big|_{surf.}$, $Fe^{2+}/Fe^{3+}\big|_{surf.}$, $Cu^{+}/Cu^{2+}/Cu^{3+}\big|_{surf.}$, $Zn^{+}/Zn^{2+}/Zn^{3+}\big|_{surf.}$, $Ce^{3+}/Ce^{4+}\big|_{surf.}$, $Mo^{4+}/Mo^{6+}\big|_{surf.}$ and $Bi^{3+}/Bi^{4+}\big|_{surf.}$ were elucidated. Moreover, detailed degradation pathways of the organic pollutants were designed and predicted, based on the various identified intermediates from LCMS/MS and MALDI-TOF/MS analysis. Lastly, the stability and the regenerability of the various synthesized catalysts were investigated through a series of consecutive reaction cycles and corresponding comparative characterization studies.