SUMMARY

The increasing contamination of water resources by persistent organic pollutants has driven the development of efficient visible-light-responsive photocatalysts with enhanced interfacial charge-transfer capability. Semiconductor-based photocatalysis has attracted considerable attention over the past decades due to its potential for the degradation of organic pollutants. Among various semiconductor materials, $BiVO_4$ has emerged as one of the most promising candidates because of its excellent visible-light absorption properties. In this study, $BiVO_4$ thin films were deposited onto fluorine-doped tin oxide (FTO) substrates and subsequently modified with a CdS heterojunction via chemical bath deposition (CBD) and an Fe_2O_3 cocatalyst via photoelectrodeposition to enhance the photoelectrochemical performance for methylene blue degradation.

The deposition methods for $BiVO_4$ thin films were evaluated through a comparison of different fabrication techniques. The results showed that the spin-coating method produced $BiVO_4$ films with more uniform morphology, higher crystallinity, and improved charge separation efficiency compared with those prepared by dip-coating. These characteristics contributed to enhanced photoelectrochemical and photocatalytic performance.

The incorporation of a CdS interlayer formed an effective Z-scheme heterojunction, while Fe_2O_3 acted as a hole-extraction cocatalyst that accelerated the surface oxidation reaction kinetics. As a result, the optimized $BiVO_4/CdS/Fe_2O_3$ thin film achieved a methylene blue degradation efficiency of 93.6% within 120 min and followed pseudo-first-order kinetics with a rate constant of 0.0222 min^{-1}. This performance represents an approximately 1.9-fold enhancement compared with pristine $BiVO_4$. Photoelectrochemical characterization revealed a significant increase in photocurrent density, reaching approximately 3.2 mA cm^{-2}, along with a substantial reduction in charge-transfer resistance relative to $BiVO_4$ and $BiVO_4/CdS$. Furthermore, the lower photoluminescence intensity indicated suppressed electron–hole recombination. These findings confirm that the formation of the Z-scheme heterojunction and the introduction of the Fe_2O_3 cocatalyst effectively enhance charge separation and carrier transport. Mechanistic analysis demonstrated that the Z-scheme system preserves a strong oxidation potential, thereby facilitating the generation of hydroxyl radicals (•OH) as the dominant reactive species responsible for methylene blue degradation. These radicals play a crucial role in breaking down chromophoric structures and promoting the continuous degradation of the dye molecules.