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Investigation of rare earth metal ions (Sm and Er) doped $CoMoO_4$ polymorphs for photocatalytic dye degradation

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Abstract

Cobalt molybdate ($CoMoO_4$) and its rare earth doped variants have emerged as promising photocatalysts for degrading dye pollutants in wastewater. The photocatalysts were prepared using a modified sol-gel method, employing ammonium heptamolybdate tetrahydrate and cobalt (II) nitrate hexahydrate as precursors. The incorporation of samarium and erbium as a dopant was hypothesized to improve the photocatalytic activity of $CoMoO_4$ by altering its band structure and creating defect sites for improved dye adsorption and degradation. The structural and optical properties of the synthesized photocatalysts were characterized using various techniques. The photocatalytic performance of $CoMoO_4$, Sm:$CoMoO_4$ and Er:$CoMoO_4$ was evaluated by monitoring the degradation of MB dye under light irradiation. The results reveal that Sm:$CoMoO_4$ and Er:$CoMoO_4$ catalysts achieve a degradation efficiencies of 99% and 97%, respectively, highlighting the potential of rare earth-doped $CoMoO_4$ as an efficient photocatalyst for the remediation of dye contaminated wastewater.

Introduction

The dye industry is an integral part of numerous industries, such as textiles, paper manufacturing, and cosmetics, and plays a critical role in producing a wide array of consumer goods [1]. However, the exponential growth of dye production has led to a pressing environmental crisis, where the dye pollutants contaminate water bodies and ecosystems, causing severe damage. The irresponsible discharge of dye-laden effluents poses dire consequences for aquatic life, human health, and ecosystem balance, making it imperative to take immediate action to address the escalating threat to environmental sustainability [2]. The primary issue is the significant challenge of effectively removing dye pollutants from wastewater. Conventional techniques, such as physical adsorption and chemical precipitation, often fail to achieve the comprehensive removal and degradation of dyes, leading to enduring environmental contamination. Therefore, innovative approaches for addressing dye pollution and facilitating efficient dye degradation have emerged as critical in environmental research and engineering [3]. Advancements in dye degradation have emphasized the potential of photocatalytic methods as promising solutions for remediation [4]. By employing the principles of photocatalysis, dye pollution can be tackled using versatile and sustainable means [[5], [6], [7], [8], [9], [10], [11]]. Synthetic dyes, widely used in various industries such as textiles, paper, plastics, and pharmaceuticals, pose a significant threat to the environment owing to their persistence and harmful effects on human health and ecosystems. Methylene blue (MB), an extensively utilized cationic dye in these industries, is known for its resistance to degradation and negative environmental impact. Therefore, developing efficient methods for removing MB from wastewater is critical for mitigating the environmental risks associated with these pollutants. Methylene blue is widely utilized in investigations of photocatalytic dye degradation owing to its distinct hue, enabling researchers to monitor its degradation through spectroscopic techniques effortlessly. Moreover, methylene blue exhibits stability under typical circumstances but is prone to degradation when subjected to photocatalysts, making it an ideal candidate for examining photocatalytic processes [3]. Some of the recent materials employed in photocatalytic dye degradation research include graphene-based nanocomposites (e.g., graphene/TiO_2) [12,13], Metal-organic frameworks (MOFs) combined with semiconductor nanoparticles (e.g., MIL-125(Ti)/CdS) [14,15], perovskite-based nanocomposites (e.g., $CsPbBr_3$ nanocrystals/TiO_2), carbon quantum dots (CQDs) combined with metal oxide nanoparticles (e.g., carbon quantum dots/ZnO) [16], and plasmonic nanomaterials integrated with semiconductor materials (e.g., gold nanoparticle-decorated Bi_2MoO_6 nanosheets) [17]. Samarium has a larger ionic radius than cobalt (Co) which is the host element of cobalt molybdate, can result in lattice strain and alter the band structure of the material, consequently leading to enhanced photocatalytic activity [[18], [19], [20], [21]]. Furthermore, the incorporation of Sm can create defect sites that serve as active sites for the adsorption and degradation of dye molecules [11,22]. Although cobalt molybdate and its Sm-doped variants show promise for dye degradation, it is essential to explore other rare earth dopants. Erbium (Er) is a promising candidate owing to its unique electronic structure and optical properties. Er ions undergo multiple electronic transitions within the 4f shell, which can facilitate efficient light absorption and up-conversion processes. Moreover, the presence of Er^{3+} ions