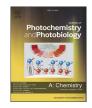


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Biowaste derived UV–Visible-NIR active Z-scheme CaO/MoS₂ photocatalyst as a low-cost, waste-to-resource strategy for rapid wastewater treatment

Gopal C. Koladia ^a, Aditi Bhole ^a, Nisha V. Bora ^b, Leena V. Bora ^{a,*}

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ABSTRACT

There is a need for industries to adopt greener strategies to minimise the environmental impact and overuse of natural resources. In the light of alarming environmental conditions, there is an expanding and progressing centre around the concept of waste to resource strategy. With this inspiration, a low-cost marine biowaste-based CaO/MoS_2 photocatalyst synthesized by ball milling is proposed with a viable green route for water remediation. The mass ratio of CaO and MoS_2 were optimized for the photocatalytic reduction of cationic methylene blue (MB) as a probe dye and an actual industrial dye wastewater. It was found that $45CaO/55MoS_2$ (45-CaMo) outperformed all the proportions including the conventionally popular TiO_2 , 70% of MB got discoloured in 10 min of exposure to natural sunlight following Langmuir-Hinshelwood model with a rate constant of 0.064 min⁻¹ and exhibiting good photo-stability. The morphology and crystallinity were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD). UV-Visible-NIR spectroscopy and calculations reveal the activity of the synthesized photocatalyst in UV, visible and IR regions with a direct Z-scheme mechanism as its probable charge modulation technique. This work offers new perspectives and directions for future research using waste-derived resources and renewable energy.

1. Introduction

The amount of wastewater and pollutant load are increasing globally due to population growth and faster urbanization. A considerable share of wastewater in impoverished metropolitan areas is directly discharged without treatment. Conventional treatment methods such as coagulation/flocculation, precipitation, etc. are not only costly but often produce additional waste pollutants.

Photocatalysis, an Advanced Oxidation Process (AOP) plays a crucial role in effectively treating wastewater without creating additional waste [1-4]. TiO $_2$ (bandgap ~ 3.2 eV) is a promising photocatalyst, but can only use about 4% of the total solar spectrum, (UV region). Thus, endeavours are made to formulise materials as photocatalysts that can be employed in the visible light region of the spectrum, which comprises 47% of the total. Noble metals, like Au, Pd, Pt and others, are frequently utilised as co-catalysts due to their high efficiencies. Their employment is, however, greatly limited by their scarcity, high-cost and probable detrition to practical applications [5-7]. Thence, development of an efficient and affordable photocatalyst is encouraged, that would offer a safe and effective photocatalytic system.

The waste-to-resource concept supports an evolutionary change in solid waste handling. In place of seeing a garbage dump as a menace, the approach motivates to use them as a valuable resource of desired raw material for further applications. Low-cost photocatalyst materials that are derived from wastes such as rice husks, pollens, shells, etc., have gained recognition for sustainable approach [8-11]. Calcium oxide (CaO) is an excellent and cost-effective photocatalyst with favourable opto-physico-chemical properties [12-14]. CaO produced from waste materials like seashells and eggshells has been employed in wastewater treatment through photocatalysis and has created fresh opportunities for sustainable chemistry [15–17]. Waste shells, are principally calcium carbonate (CaCO3) and a fantastic natural source of CaO. Seashellsderived-CaO has demonstrated outstanding support, strong photocatalytic activity, and enhanced charge separation efficiency [18]. MoS₂ also exhibits exciting photocatalytic performance due to its good bonding and stability, small bandgap making it more active upon light radiation, favourable chemical structure and ability of heterojunctioning with other matrix films [19-22]. As compared to single-component photocatalysts, composite ones have made tremendous advancements in the recent past and hence, we introduce a coupling of CaO/MoS₂

E-mail address: leena.bora@nirmauni.ac.in (L.V. Bora).

^a Department of Chemical Engineering, Institute of Technology, Nirma University, Ahmedabad 382481, India

^b Department of Mechanical Engineering, L.D. College of Engineering, Ahmedabad 382481, India

^{*} Corresponding author.