

TRANSITION METALS AND ITS MODIFIED FORMS AS EFFICIENT PHOTOCATALYSTS FOR ENERGY AND ENVIRONMENTAL APPLICATIONS

Abstract

Delving into the pressing global demand for sustainable energy and environmental solutions, the focus lies on the field of photocatalysis. The promising potential of transition metal-based photocatalysts and their modified forms for solar energy conversion and environmental pollution remediation is thoroughly explored. Transition metal oxides, sulfides, and metal-organic frameworks (MOFs) are extensively studied due to their exceptional optoelectronic properties, band gap structures, and redox activity, making them highly efficient in harnessing solar energy. Additionally, the utilization of abundant, low-cost elements in these materials presents attractive alternatives to precious metal-based catalysts, enabling practical large-scale applications. The chapter highlights various strategies, including surface engineering, heterostructure formation, and doping, that researchers have employed to enhance the photocatalytic activity and extend the photo response into the visible light region. It covers a wide range of photocatalytic applications, such as hydrogen generation, carbon dioxide reduction, water purification, and pollutant degradation, showcasing the versatility and efficacy of transition metal-based photocatalysts in addressing critical energy and environmental challenges. The comprehensive overview aims to provide valuable insights for researchers, scientists, and engineers in the fields of energy and environmental technologies, inspiring further research and innovation for a cleaner, sustainable future powered by solar energy and free from environmental pollutants.

Keywords: Photocatalysis, Nanomaterials, Transition metals, Metal oxide, Metal organic framework, Metal sulfide, Hydrogen evolution, Water splitting

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I. INTRODUCTION

The urgent need for sustainable energy and environmental solutions has spurred significant research in the field of photocatalysis. Photocatalysis, a process that utilizes light energy to drive chemical reactions, holds immense promise for addressing pressing global challenges such as solar energy conversion and environmental pollution[1]. Transition metal-based photocatalysts, with their unique structural and electronic properties, have emerged as highly promising candidates for these applications[2]. Transition metal oxides, sulfides, and metal-organic frameworks (MOFs) are some of the most extensively studied materials in the realm of photocatalysis[3]–[5]. Their exceptional optoelectronic properties, band gap structures, and redox activity make them highly efficient in harnessing solar energy and promoting various photochemical reactions. Moreover, these materials often possess abundant, low-cost, and earth-abundant elements, making them attractive alternatives to precious metal-based catalysts for large-scale applications.

In recent years, researchers have explored various strategies to modify the properties of transition metal-based photocatalysts, aiming to enhance their performance and selectivity. Surface engineering, heterostructure formation, and doping with elements such as nitrogen and metals have been employed to optimize the photocatalytic activity and extend the photo response of these materials into the visible light region[6], [7]. This book chapter explores the recent advances and applications of transition metal-based photocatalysts and their modified forms in the realm of energy conversion and environmental remediation. It covers a wide range of topics, including the synthesis and characterization of transition metal oxides, sulfides, and Metal organic frameworks (MOFs), and their tailored modifications to improve photocatalytic performance. Various photocatalytic applications, such as hydrogen generation, carbon dioxide reduction, water purification, and pollutant degradation, will be discussed, highlighting the potential of these materials in addressing critical energy and environmental challenges[8].

The chapter aims to provide a comprehensive overview of the current state-of-the-art in transition metal-based photocatalysts and their modified forms, offering valuable insights for researchers, scientists, and engineers working in the fields of energy and environmental technologies. By harnessing the remarkable properties of transition metal materials, we can pave the way for a sustainable future, where solar energy becomes a clean and abundant source of power and environmental pollutants are efficiently removed, ensuring a cleaner and healthier planet for generations to come.

In recent years, transition metal-based photocatalysts have undergone significant advancements in terms of synthesis techniques and structural design, enabling precise control over their morphologies and properties[9]. The emergence of nanostructured photocatalysts has opened up new avenues for enhancing light absorption, charge separation, and catalytic activity, as well as improving the overall efficiency of the photocatalytic process[10]. One of the key challenges in photocatalysis is the limited utilization of solar energy, particularly in the visible light region[11]. To address this limitation, researchers have focused on tailoring the band gap of transition metal photocatalysts through band engineering and heterostructure formation[12]. By combining different transition metal oxides, sulfides, or semiconductors, novel heterojunctions can be engineered to promote efficient charge transfer across interfaces and extend the absorption spectrum to visible light wavelengths[13].

Furthermore, the incorporation of dopants and co-catalysts into transition metal-based photocatalysts has proven to be a powerful strategy for enhancing their photocatalytic activity and selectivity[14], [15]. Doping with elements like nitrogen, sulfur, or metals introduces new energy levels within the band gap, facilitating charge carrier separation and reducing recombination rate[16]. Co-catalysts, on the other hand, serve as active sites for specific reactions, accelerating the kinetics of photocatalytic processes and improving overall efficiency. The applications of transition metal and its modified form photocatalysts are extensive. In energy conversion, these materials hold great promise for solar-driven water splitting to produce hydrogen, a clean and renewable fuel. The photocatalytic reduction of carbon dioxide to valuable hydrocarbons and chemical feedstocks also offers a sustainable solution for mitigating greenhouse gas emissions[17], [18]. Moreover, transition metal-based photocatalysts exhibit exceptional potential for environmental applications, such as the degradation of organic pollutants, disinfection of water, and removal of heavy metals, contributing to cleaner water and air[19].

In this book chapter, we will delve into the recent developments in transition metal-based photocatalysts and their modified forms, exploring the underlying principles and mechanisms that govern their photocatalytic performance. The synthesis methods, structural characterization, and optimization strategies will be discussed to provide a comprehensive understanding of these materials' design and engineering. Furthermore, the chapter will present case studies of various photocatalytic applications, showcasing the versatility and efficacy of transition metal and its modified form photocatalysts in real-world scenarios.

Overall, this chapter seeks to shed light on the remarkable potential of transition metal-based photocatalysts as key players in addressing global energy and environmental challenges. By elucidating the underlying principles and recent advances in this field, we aim to inspire further research and innovation in the development of efficient, scalable, and sustainable photocatalytic technologies for a cleaner and greener future.

II. TRANSITION METAL OXIDES AS PHOTOCATALYSTS

Transition metal oxides are commonly used as photocatalysts due to their unique structural and electronic properties, Few of which it makes them stand out are: Optoelectronic properties, Band gap structure, Photostability, Redox activity, Versatility, Abundance and low cost and Compatibility with environmental conditions. Transition metal oxides have a range of energy level within their electronic structure including conduction and valence bands that are suitable for absorbing visible lights which means they can utilize a broader range of solar spectrum compared to other materials, making them efficient in harnessing solar energy[20]. Many Transition metal oxides (TMO) have a suitable band gap structure which refers to the energy difference between the valence and conduction band. A narrow band gap enables absorption of visible light while a wider band gap allows the catalyst to generate highly reactive species such as hydroxyl radical which are useful of various photocatalytic reaction[21]. These materials are generally stable under light irradiation and can withstand harsh reaction conditions. They are less prone to photo corrosion or degradation compared to other photocatalytic materials ensuring longer operational life time[22]. Transition metals in their different oxidation states can undergo reversible redox reactions. This property allows them to act as electron acceptors or donors during photocatalytic processes, facilitating the generation and transfer of charge carriers (electrons and holes) for the desired reactions[23].

Transition metals such as titanium (Ti), zinc (Zn), iron (Fe), and tungsten (W) are abundant in the Earth's crust, making them cost-effective compared to other rare or precious metal-based catalysts. This availability and affordability make transition metal oxides attractive for large-scale applications[24]. These metal oxides exhibit diverse catalytic functionalities, enabling them to perform a wide range of photocatalytic reactions. They can be utilized for water splitting, pollutant degradation, carbon dioxide reduction, and other environmentally beneficial processes[25]. And also Transition metal oxides are often chemically stable and can operate under a wide range of pH conditions, temperatures, and atmospheric environments, making them adaptable for various practical applications[26].

Photocatalytic performance is mainly dependent on many factors such as Morphology, crystalline phase, crystal structure, composition, intrinsic defects (oxygen vacancy). The final photocatalytic performance of such materials are directly influenced by the presence of oxygen. It is of utmost importance to control size shape and crystallinity of materials which directly influence charge carriers and in turn final photocatalytic activity[27].

High photostability, chemical inertness, and a relatively high oxidation efficiency under UV light ($\lambda < 387$ nm) are all characteristics of titanium dioxide. The energy of UV light exceeds the bandgap of TiO_2 (from 3.0 to 3.2 eV for the rutile and anatase forms, respectively). This TiO_2 is a semiconductor that is often utilised in heterogeneous photocatalysis and is well known. However, in order to use sustainable solar energy, photocatalysts with high reactivity under visible light ($\lambda > 400$ nm) are needed for the widespread application of metal oxide-based photocatalysis[28].

Mohd Fazil et al. synthesized highly crystalline and Tetragonal structured TiO_2 and Sr doped TiO_2 nanocatalyst using Low temperature Hydrothermal method. Studies were carried out to elucidate different properties of the as synthesized materials which investigated the characteristics of TiO_2 nanoparticles with varying levels of Sr doping. The pristine TiO_2 nanoparticles had high surface areas ranging from 141.16 to 182 $\text{m}^2 \text{g}^{-1}$. The Sr-doped nanoparticles (1%, 2.5%, and 5% Sr doping) had slightly larger average particle sizes, ranging from 11.1 to 13 nm. Among the Sr-doped nanoparticles, the 1% Sr-doped TiO_2 nanoparticles showed the most promising results. They exhibited a higher hydrogen production rate of 26.30 $\text{mmolg}^{-1}\text{cat}$, indicating their effectiveness as photocatalysts. The electrocatalytic properties of the Sr-doped TiO_2 nanoparticles were also evaluated for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in different electrolytic solutions. In both 0.5 N H_2SO_4 and 0.1 N KOH electrolytes, the 1% and 5% Sr-doped TiO_2 nanoparticles demonstrated the highest current densities for HER and OER. Overall, these findings highlight the improved photocatalytic and electrocatalytic activities of Sr-doped TiO_2 nanoparticles, particularly the 1% Sr-doped variant. They exhibited higher hydrogen production and achieved significant current densities for both HER and OER, indicating their potential for various applications[29]

Iron oxide nanoparticles and their composites have gained considerable attention in the field of wastewater remediation. These nanoparticles, including magnetite (Fe_3O_4) and hematite (Fe_2O_3), are being increasingly explored for their ability to effectively remove various pollutants from water. In a work Bedabratasaha et al. synthesized iron oxide nanoparticles, with an average size of 20-40 nm and a surface area of around 70 $\text{m}^2 \text{g}^{-1}$, and employed it for the targeted adsorption of specific dyes containing hydroxyl groups from

aqueous solutions. The nanoparticles selectively capture these dyes based on their chemical properties. In this work Magnetite nanoparticles have been employed effectively in the elimination of chlorinated pesticides from contaminated water. Pesticides such as lindane, hexachlorocyclohexane (α -HCH and γ -HCH), dieldrin, 2,4-dichlorophenoxyacetic acid (2,4-D), and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) have been successfully targeted for removal using these nanoparticles. The chemical structure of these chemicals affects how well they adhere to the iron oxide nanoparticles. Particularly, compared to non-hydroxylated dyes like methyl orange, methylene blue, and methyl red, organic dyes with hydroxyl functional groups, such as Eriochrome Black T, Bromophenol Blue, Bromocresol Green, and Fluorescein, show a preference for adsorption onto magnetite nanoparticles.[30]

III. METAL ORGANIC FRAMEWORKS AS PHOTOCATALYSTS

Metal-organic frameworks (MOFs) have emerged as promising photocatalytic materials due to their tunable structure, high surface area, and unique properties[31]. MOFs are composed of metal ions or clusters coordinated to organic ligands, which can be tailored to absorb specific wavelengths of light, enabling them to harness a broad range of light energies. Upon light absorption, MOFs generate electron-hole pairs, and their well-defined structures facilitate efficient charge separation, minimizing electron-hole recombination. The metal centers within MOFs serve as catalytic active sites for various reactions, including water splitting, carbon dioxide reduction, pollutant degradation, and organic synthesis[32]–[37]. Furthermore, MOFs can host guest molecules within their pores, enhancing catalytic performance and selectivity[38]. Remarkably stable under photocatalytic conditions, MOFs can be designed with robust linkers and metal centers, offering potential for sustainable and recyclable catalytic processes. Overall, the tunable nature, high surface area, efficient charge separation, catalytic active sites, guest molecule interactions, stability, and recyclability make MOFs promising candidates for a wide range of photocatalytic applications.

In a study Lania A siddig et al. developed a new trinuclear manganese cluster-based manganese metal-organic framework (Mn-MOF) known as UAEU-50. This adopted a 2D structure with a hexagonal layer net (hxl), which led to excellent thermal stability and chemical stability. It was found that the synthesised material when employed for the photocatalytic activity showed excellent results in cycloaddition of CO₂ to various epoxides to create cyclic carbonates. The novel MOF displayed a band gap value of 3.04 eV and is one of the earliest instances of Mn-MOFs employed for the CO₂ cycloaddition purpose, and it exhibited impressive CO₂ conversion rate of up to 90% in the visible light area at ambient circumstances[39].

In a study Xiaoyu He et al. designed a highly efficient MOF-based photocatalyst called Fe/Ti-BPDC for converting CO₂ under visible light. The catalyst demonstrated exceptional performance, achieving an impressive yield of 703.9 $\mu\text{mol g}^{-1} \text{h}^{-1}$ and an outstanding selectivity of over 99.7% in the CO₂ photoreduction to formic acid (HCOOH). The catalyst's remarkable capabilities can be attributed to the cooperative coordination between Ti-oxo clusters, chelating ligands, and atomically dispersed Fe active sites, leading to a 'dual-optimization' effect, which involves two critical aspects: sustaining a continuous supply of photogenerated electrons for catalysis and enhancing the activation of CO₂. The atomically dispersed Fe active sites play a crucial role in achieving high selectivity for the formation of HCOOH and also enable rapid CO₂ activation due to their strong affinity for

oxygen. The success of this study confirms the feasibility and versatility of the dual-benefit design strategy[40].

Y.B.N. Tran et al. developed a series of isostructural Metal-Organic Frameworks (MOFs) referred to as M-MOF-184, with M representing different metals like Mg, Ni, Co, Zn, Cu, and Fe. In this series, the Co-based framework demonstrated the highest capacity for adsorbing CO₂ at low pressure (73 cm³ g⁻¹ at 800 Torr and 298 K). On the other hand, Ni-MOF-184 exhibited the highest energy of adsorption for CO₂ (36 kJ mol⁻¹). Impressively, Zn-MOF-184 exhibited outstanding performance as a catalyst in the CO₂ cycloaddition reaction, achieving a remarkable 96% conversion rate, 86% selectivity, and 82% yield under mild reaction conditions (solvent-free, using balloon pressure of CO₂, at 80 °C for 6 hours). It's noteworthy that the catalytic activity of Zn-MOF-184 surpassed that of both homogeneous and heterogeneous catalysts, the M-MOF-74 (M = Mg, Co, Zn) series, and other Zn-based MOFs. The researchers also conducted FTIR analysis on these MOFs after acetonitrile adsorption to determine the relative acidity and basicity of four different M-MOF-184 variants. The outcomes revealed that the Zn sites with Lewis acid characteristics in the Zn-MOF-184 structure, along with the basic 2-oxidobenzoate anions originating from the Co framework, demonstrated the strongest acidity and basicity, respectively. These findings aligned well with the exceptional catalytic activity witnessed in Zn-MOF-184 during the CO₂ cycloaddition reaction, as well as the remarkable uptakes of both CO₂ and acetonitrile observed in Co-MOF-184[41].

IV. TRANSITION METAL SULFIDES AS PHOTOCATALYSTS

In a study led by A. Puttarangappa et al., a novel photocatalyst system was developed for efficient water splitting to produce hydrogen gas (H₂). The researchers combined 2D tin(IV) sulfide (SnS₂) ultrathin nanosheets as co-catalysts with 1D cadmium sulfide (CdS) nanorods. This innovative design served two main purposes: firstly, it passivated the physiochemical properties of CdS, reducing defects and recombination centers on the surface, thereby improving the catalytic performance. Secondly, the incorporation of SnS₂ nanosheets significantly enhanced the H₂ evolution activity, leading to approximately 9 times higher H₂ generation rate compared to pure CdS nanorods. Through optimization, the researchers found that a SnS₂ loading amount of 5 wt% on the CdS nanorods yielded the highest H₂ production rate of 20.2 mmol h⁻¹ g⁻¹. Additionally, they investigated the impact of a scavenger, lactic acid (LA), on the H₂ generation rate and identified that using 3 ml of LA was optimal. Remarkably, the CdS/SnS₂ photocatalyst exhibited excellent stability, maintaining its H₂ evolution rate for over 30 hours without any degradation. These findings hold great promise for the advancement of efficient and stable photocatalysts, bringing us closer to harnessing solar energy for sustainable hydrogen fuel production[42].

In the research conducted by Wei Chen et al. they developed a series of innovative hybrid photocatalysts named WO_{2.72}/ZnIn₂S₄ (referred to as WOZIS) with the purpose of efficiently breaking down tetracycline hydrochloride (TCH) using visible light, all without the necessity of solid-state electron mediators. These hybrid photocatalysts consisted of one-dimensional (1D) WO_{2.72} (WO) nanorods and two-dimensional (2D) ZnIn₂S₄ (ZIS) nanosheets. This novel design aimed to facilitate the degradation of tetracycline hydrochloride under visible light exposure. By utilizing an in-situ growth technique under hydrothermal conditions, the researchers prepared various WOZIS hybrid photocatalysts with

varying molar ratios of WO to ZIS. The results showed that all WOZIS hybrid photocatalysts exhibited a significant enhancement in their ability to break down TCH through photocatalysis. Particularly, the WOZIS-1 sample, characterized by a 1:1 molar ratio of WO to ZIS, showcased the most remarkable photocatalytic performance. Within a mere 60 minutes of exposure to visible light, it managed to degrade an impressive 97.3% of TCH. This outstanding performance was attributed to the Z-scheme charge separation mechanism, which was made possible by the close interaction and well-aligned band potentials between the 1D WO_{2.72} nanorods and 2D ZnIn₂S₄ nanosheets within the hybrid structure. This Z-scheme mechanism efficiently harnessed the energy from visible light and effectively separated the generated electron-hole pairs, preventing them from recombining and thereby significantly enhancing the overall efficiency of photocatalysis. By ingeniously integrating the unique properties of 1D WO nanorods and 2D ZIS nanosheets in the WOZIS hybrid photocatalyst, a synergistic effect was achieved. This synergistic effect resulted in a highly effective and stable system for breaking down tetracycline hydrochloride. This advancement holds potential applications in addressing challenges related to wastewater treatment and environmental remediation[43].

Lei Lei Li et al. successfully synthesized porous MoS₂/CdS heterostructures via a one-pot solvothermal method. The heterostructures consisted of big spheres self-assembled by sub-nanospheres (approximately 3.6 nm in size). These heterostructures displayed an exceptional H₂ evolution rate of 37.31 mmol g⁻¹ h⁻¹, which was 162 times higher than the pristine CdS. The impressive photocatalytic performance was attributed to the formation of well-defined heterostructures that facilitated charge transport and separation. The presence of amorphous MoS₂ further contributed to the remarkable performance by reducing H₂ overpotential and providing a higher number of active sites. Additionally, the MoS₂/CdS nanosphere heterostructures demonstrated good stability, maintaining their catalytic activity over four 24-hour cycles. This study highlights the potential of these heterostructures as efficient and stable photocatalysts for hydrogen evolution[44].

In their study, Lixiang Zhang et al. developed a novel photocatalyst for efficient Cr(VI) reduction under visible light using direct Z-scheme heterojunctions of CdS/N-CoSx nano composites. To enhance the photocatalytic activity, they loaded CdS onto CoSx and doped nitrogen (N) into the CoSx structure through N₂ plasma treatment. The N₂ plasma treatment served a dual purpose. It facilitated the covalent doping of N elements into CoSx by forming Co-N bonds and it also regulated the surface wettability, conductivity, and Fermi level of the material. Compared to the photocatalysts without N₂ plasma treatment, the direct Z-scheme heterojunctions exhibited significantly improved photocatalytic performance. The specific conditions of the N₂ plasma treatment were crucial for optimizing the photocatalytic efficiency. The experiment revealed that the photocatalyst treated with N₂ plasma for 5 minutes and with an 8:1 M ratio (presumably referring to the molar ratio of CoSx to CdS) displayed the highest photocatalytic performance, achieving a remarkable 100% efficiency in Cr(VI) reduction within just 25 minutes of visible light illumination. This research demonstrates the effectiveness of constructing direct Z-scheme heterojunctions of CdS/N-CoSx nano composites through N₂ plasma treatment for enhanced photocatalytic activity. The tailored heterojunction design with N-doping and controlled ratios of CoSx to CdS provides valuable insights for developing highly efficient photocatalysts for environmental remediation and other applications[45].

In the study conducted by Murthy Muniyappa et al., they explored the use of cocatalyst-free nickel sulfide (NiS) nanostructures as efficient photocatalysts for hydrogen generation. NiS is considered highly active, inexpensive, and abundant, making it a promising candidate for photocatalytic applications. The researchers synthesized stable NiS-a and NiS-b phases through the solvothermal method, by adjusting the water to ethanol ratio during the synthesis process. The resulting samples exhibited a hexagonal and rhombohedral crystal structure with high phase purity, indicating the successful formation of the desired NiS phases. The optical bandgap of the NiS nanostructures was measured to be 1.83 eV, which is considered favorable for hydrogen generation through photocatalysis. In the photocatalytic tests, the NiS-a phase demonstrated superior performance in hydrogen generation compared to the NiS-b phase. Specifically, the NiS-a sample achieved a hydrogen generation rate of 13.413 mmol h⁻¹ g⁻¹ within a 4-hour duration, indicating its high activity for the photocatalytic process. Moreover, the NiS-a and NiS-b nanostructures exhibited good stability during the photocatalytic process, which is essential for practical applications. Based on these results, the study suggests that the synthesized NiS-a and NiS-b nanostructures could be considered as preferable options for photocatalytic hydrogen generation compared to binary or ternary compounds. The absence of a cocatalyst makes these materials more cost-effective and simplifies the photocatalyst preparation process, further enhancing their potential for scalable and environmentally friendly hydrogen production through photocatalysis[46].

V. CONCLUSION

In summary, this book chapter offers a comprehensive understanding of the recent advances and applications of transition metal-based photocatalysts and their modified forms. By elucidating the underlying principles, synthesis techniques, and structural design, the chapter highlights the potential of these materials in addressing critical energy and environmental challenges. From tailoring band gaps to incorporating dopants and cocatalysts, researchers have successfully enhanced photocatalytic performance. The versatility of transition metal-based photocatalysts is showcased in various applications, from hydrogen generation to pollutant degradation. With an emphasis on sustainability and practicality, the chapter emphasizes the promise of transition metal-based photocatalysts in paving the way for a cleaner and greener future powered by solar energy. Researchers, scientists, and engineers in the fields of energy and environmental technologies will find this chapter's comprehensive insights invaluable, inspiring further research and innovation for a sustainable and eco-friendly world.

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