

Rare-Earth Doped Transition Metal–Organic Framework (RE–TM–MOF) for Efficient Photo catalytic Hydrogen Evolution

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Abstract:

The core structure of the rare-earth doped transition metal–organic framework (RE–TM–MOF) incorporating Ru-doped Ag within a phenanthroline framework can be described as a multifunctional hybrid system in which each component plays a synergistic role in enhancing photocatalytic hydrogen evolution. At the center of the architecture, a Ru (phen)₃²⁺ complex acts as an efficient photosensitizer, owing to its strong metal-to-ligand charge transfer (MLCT) transitions and excellent visible-light absorption capability. This Ru–phenanthroline unit is either encapsulated within or anchored onto the MOF framework through coordination interactions with the phenanthroline ligands, which serve as π -conjugated organic linkers facilitating electron transport. Surrounding this core, silver (Ag) functions as the primary transition metal node, forming coordination bonds with oxygen or nitrogen donor atoms to construct the MOF network. The presence of Ag not only provides catalytic active sites but also contributes to enhanced charge mobility and plasmonic light absorption effects. Simultaneously, rare-earth ions such as Nd³⁺ or Ce³⁺ are incorporated into the framework as dopants, introducing discrete f-orbital energy levels that act as charge trapping centers, thereby suppressing electron–hole recombination and prolonging charge

carrier lifetimes. Structurally, the system can be viewed as a core–shell-like arrangement, where the Ru–phenanthroline complex forms the photoactive core, the Ag-based nodes act as electron mediators, and the RE-doped MOF constitutes the outer porous framework. Upon light irradiation, excited electrons generated in the Ru center are efficiently transferred through the Ag nodes and stabilized by the rare-earth ions before participating in proton reduction to produce hydrogen. This integrated design enables improved light harvesting, efficient charge separation, and accelerated electron transfer, making the RE–TM–MOF system highly effective for photo catalytic hydrogen evolution.

Keywords

Photocatalysis; Hydrogen Evolution; MOFs; Rare-Earth Doping; Charge Separation

Introduction:

The rapid depletion of fossil fuels, coupled with escalating environmental concerns such as global warming and air pollution, has driven the urgent need for sustainable and clean energy alternatives. Among the various energy carriers, hydrogen (H_2) has emerged as a highly promising candidate due to its high gravimetric energy density and environmentally friendly nature, producing only water as a combustion by-product. In recent years, photocatalytic water splitting has attracted significant attention as an efficient and green method for hydrogen production, as it utilizes abundant solar energy to drive chemical reactions. This approach not only addresses energy scarcity but also contributes to reducing carbon emissions, thereby supporting the transition toward a carbon-neutral economy.

Photocatalytic hydrogen evolution involves the absorption of photons by a semiconductor material, leading to the generation of electron–hole pairs. These charge carriers participate in redox reactions, where photogenerated electrons reduce protons to produce hydrogen, while holes oxidize water to

generate oxygen [1]. However, conventional semiconductor photocatalysts such as TiO₂, ZnO, and CdS face several limitations, including narrow light absorption ranges, rapid recombination of charge carriers, and insufficient catalytic efficiency. These challenges have motivated researchers to explore advanced materials with improved optical and electronic properties for enhanced photocatalytic performance.

In this context, Metal–Organic Frameworks (MOFs) have emerged as a new class of porous crystalline materials with immense potential in photocatalysis. MOFs are composed of metal ions or clusters coordinated with organic ligands to form highly ordered three-dimensional structures. Their exceptional surface area, tunable pore size, and structural diversity make them highly suitable for catalytic applications. Importantly, the modular nature of MOFs allows precise control over their chemical composition and electronic structure, enabling the design of tailored photo catalysts [2]. Furthermore, MOFs can incorporate functional organic linkers that act as light-harvesting units, thereby enhancing photon absorption and facilitating charge transfer processes.

Despite these advantages, pristine MOFs suffer from inherent drawbacks such as poor electrical conductivity and rapid recombination of photo generated electron–hole pairs, which significantly limit their photo catalytic efficiency. To address these issues, several modification strategies have been developed, including metal doping, hetero junction formation, ligand engineering, and the incorporation of co-catalysts. Among these approaches, the incorporation of transition metals (TMs) into MOFs has proven to be particularly effective. Transition metals such as nickel (Ni), cobalt (Co), iron (Fe), and copper (Cu) provide active catalytic sites for hydrogen evolution reactions (HER) and facilitate efficient electron transfer due to their partially filled d-orbitals [3].

In recent years, the integration of rare-earth (RE) elements into MOFs has emerged as a powerful strategy to further enhance photo catalytic performance. Rare-earth ions, including lanthanides such as cerium (Ce), neodymium (Nd), europium (Eu), and lanthanum (La), possess unique electronic

configurations characterized by partially filled 4f orbitals. These 4f orbitals impart distinctive optical and electronic properties, including sharp absorption bands, long excited-state lifetimes, and efficient energy transfer capabilities [4]. As a result, rare-earth-based MOFs exhibit enhanced light-harvesting ability and improved photo catalytic activity.

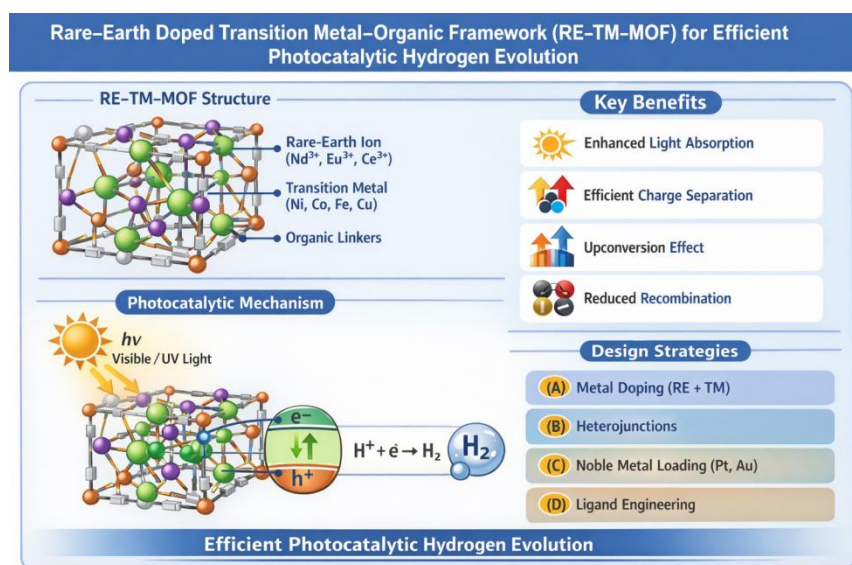
One of the key advantages of rare-earth doping is its ability to improve charge separation and suppress electron–hole recombination. Rare-earth ions can act as electron or hole trapping centers, thereby prolonging the lifetime of charge carriers and increasing their participation in photo catalytic reactions. Additionally, certain rare-earth elements exhibit upconversion properties, enabling the conversion of low-energy photons (near-infrared) into higher-energy photons (visible or UV), which can be utilized for photo catalysis [5, 6]. This feature significantly enhances solar energy utilization efficiency and broadens the spectral response of the photocatalyst.

The combination of rare-earth elements with transition metal centers in MOFs, forming Rare-Earth Doped Transition Metal–Organic Frameworks (RE–TM–MOFs), represents a synergistic approach to optimizing photo catalytic hydrogen evolution. In such hybrid systems, transition metals serve as active catalytic sites for hydrogen evolution, while rare-earth ions enhance light absorption and regulate charge carrier dynamics. The organic linkers contribute by facilitating electron transport and stabilizing the framework structure. This synergistic interaction significantly improves photo catalytic efficiency compared to single-component systems.

Recent studies have demonstrated that RE–MOF-based composites can achieve remarkable hydrogen evolution performance when combined with semiconductor materials to form hetero junction systems. For example, rare-earth MOF composites integrated with CdZnS nanoparticles have shown significantly enhanced hydrogen production rates due to improved charge separation and interfacial electron transfer. Such systems can achieve hydrogen evolution rates as high as several thousand $\mu\text{mol g}^{-1} \text{h}^{-1}$, highlighting their potential for practical applications [7].

Moreover, recent advances in lanthanide-based MOFs (Ln–MOFs) have provided deeper insights into the design and optimization of photo catalysts for hydrogen production. These studies emphasize the importance of controlling factors such as metal coordination environment, ligand functionality, and electronic structure to enhance photo catalytic efficiency. Additionally, emerging strategies such as defect engineering, dynamic structural modulation, and the construction of Z-scheme hetero junctions have further improved charge separation and catalytic activity [8].

Despite the significant progress achieved in the development of RE–TM–MOFs, several challenges remain. These include the stability of MOFs in aqueous environments, potential leaching of metal ions, and the high cost associated with certain rare-earth elements. Furthermore, large-scale synthesis and practical implementation of these materials require further investigation. Addressing these challenges is crucial for the commercialization of MOF-based photo catalysts in hydrogen production technologies [9, 10].



3. Role of Rare-Earth Doping in RE–TM–MOFs

Rare-earth (RE) doping plays a pivotal role in enhancing the photo catalytic performance of transition metal–organic frameworks (TM–MOFs), particularly for hydrogen evolution reactions.

Rare-earth elements such as cerium ($\text{Ce}^{3+}/\text{Ce}^{4+}$), neodymium (Nd^{3+}), europium (Eu^{3+}), and lanthanum (La^{3+}) possess unique electronic configurations characterized by partially filled 4f orbitals. These orbitals are shielded by outer 5s and 5p electrons, resulting in sharp and well-defined energy levels that are highly beneficial for light absorption and electronic transitions [11, 12]. When incorporated into MOF structures, RE ions introduce intermediate energy states within the band gap, thereby extending light absorption into the visible and near-infrared regions.

One of the primary advantages of RE doping is its ability to act as a charge trapping center. During photo catalysis, photo generated electrons and holes tend to recombine rapidly, limiting efficiency. RE ions effectively capture these charge carriers, prolonging their lifetime and facilitating their participation in redox reactions. Furthermore, certain rare-earth ions exhibit upconversion properties, where low-energy photons are converted into higher-energy photons, enabling the utilization of a broader solar spectrum. This significantly enhances solar energy conversion efficiency.

In addition, RE doping introduces structural defects and distortions within the MOF framework, which can create additional active sites for catalytic reactions. These defects improve reactant adsorption and facilitate faster reaction kinetics [13, 14]. Overall, the incorporation of rare-earth elements not only improves optical properties but also enhances charge dynamics and catalytic efficiency, making RE–TM–MOFs highly promising for photo catalytic hydrogen production.

4. Photo catalytic Mechanism of RE–TM–MOFs

The photo catalytic hydrogen evolution mechanism in RE–TM–MOFs involves a series of well-coordinated steps including light absorption, charge generation, separation, and surface redox reactions. Upon irradiation with light energy ($h\nu$), the photosensitizer component, typically a Ru–phenanthroline complex or conjugated organic linker, absorbs photons and becomes excited. This

excitation leads to the promotion of electrons from the valence band (VB) to the conduction band (CB), leaving behind holes in the VB.

The presence of transition metal centers such as Ag, Ni, or Co facilitates the transfer of these excited electrons. These metals act as electron mediators, allowing efficient migration of electrons through the MOF structure [15]. Simultaneously, rare-earth ions serve as electron or hole traps, preventing recombination and extending the lifetime of charge carriers. This synergistic interaction ensures efficient charge separation, which is crucial for photo catalytic activity.

The photo generated electrons are subsequently transferred to the catalytic active sites, where they reduce protons (H^+) to form hydrogen gas (H_2). Meanwhile, the holes in the valence band participate in oxidation reactions, typically involving sacrificial agents or water molecules. The efficiency of this process depends on factors such as band alignment, charge mobility, and surface active sites [16].

5. Design Strategies for High-Performance RE–TM–MOFs

The design of efficient RE–TM–MOFs requires careful consideration of structural and electronic parameters. One of the most effective strategies is dual metal doping, where both rare-earth and transition metal ions are incorporated into the MOF framework. This approach creates synergistic interactions that enhance catalytic activity and charge transport properties.

Another important strategy is ligand engineering, where organic linkers such as phenanthroline, porphyrins, or amino-functionalized ligands are used to improve light absorption and electron transfer. These ligands provide π -conjugated systems that facilitate efficient charge mobility within the framework. Additionally, heterojunction formation with semiconductor materials like $g-C_3N_4$ or CdS can further improve charge separation by creating built-in electric fields at the interface [17].

The incorporation of plasmonic metals such as Ag or Au is another promising approach. These metals exhibit surface Plasmon resonance (SPR), which enhances light absorption and generates hot electrons that contribute to photo catalysis. Furthermore, defect engineering can be employed to introduce vacancies or distortions in the MOF structure, creating additional active sites and improving catalytic efficiency. Optimizing synthesis parameters such as temperature, pH, and precursor concentration is also crucial for achieving the desired morphology and crystallinity. By combining these strategies, researchers can design RE–TM–MOFs with superior photo catalytic performance [18, 19].

6. Advantages of RE–TM–MOF Systems

RE–TM–MOFs offer several advantages over conventional photo catalysts, making them highly attractive for hydrogen evolution applications. One of the most significant advantages is their high surface area and porosity, which provide abundant active sites for catalytic reactions. This enhances reactant adsorption and improves overall reaction efficiency. Another key advantage is their tunable electronic structure. By varying the metal nodes, rare-earth dopants, and organic ligands, the band gap of MOFs can be precisely controlled to optimize light absorption and charge transfer properties. This level of tunability is not easily achievable in traditional semiconductor materials.

The presence of rare-earth ions further enhances charge separation and reduces recombination losses, leading to improved photo catalytic efficiency. Additionally, the incorporation of transition metals provides efficient catalytic sites for hydrogen evolution, ensuring rapid reaction kinetics. RE–TM–MOFs also exhibit structural versatility and stability, allowing them to be tailored for specific applications. Their ability to integrate multiple functionalities, such as light harvesting,

charge transport, and catalysis, within a single framework makes them highly efficient and multifunctional materials.

7. Challenges and Limitations

Despite their promising properties, RE–TM–MOFs face several challenges that limit their practical application. One of the major issues is stability in aqueous environments, as many MOFs are prone to degradation when exposed to water or under prolonged irradiation. This can lead to loss of structural integrity and reduced catalytic performance.

Charge recombination, although reduced by RE doping, still remains a concern in some systems [20]. Furthermore, the low electrical conductivity of MOFs can limit electron transport, affecting overall efficiency. Table 1 shows comparison of Photo catalytic study of Nanomaterials. There is also a need for better understanding of the mechanistic pathways and the role of each component in the photo catalytic process. Addressing these challenges requires the development of more stable MOF structures, cost-effective synthesis methods, and advanced characterization techniques to better understand and optimize their performance.

Table -1 Comparison of Photo Catalytic Studies of Nanomaterials.

Material/System	Light Absorption	Charge Separation	Catalytic Activity	Limitations	Reference
TiO ₂ , ZnO (Conventional Semiconductors)	UV region only	Poor	Moderate	Fast recombination, narrow spectrum	[1]
CdS-based Photocatalysts	Visible light	Moderate	Good	Photocorrosion, instability	[2]
Pristine MOFs	Tunable but limited	Poor	Low	Low conductivity, recombination	[4],[5]

TM–MOFs (Ni, Co, Fe, Cu)	Improved	Moderate	Good	Limited light harvesting	[6]
RE–MOFs	Extended (Visible + NIR)	Good	Moderate	High cost, synthesis complexity	[7],[8]
MOF-Semiconductor Composites	Broad spectrum	Very Good	High	Interface issues	[9]
RE–TM–MOF (This Work)	Broad (UV–Vis–NIR)	Excellent	Very High	Cost, stability issues	This Work

8. Future Perspectives

The future of RE–TM–MOFs in photo catalytic hydrogen evolution lies in the development of innovative design strategies and advanced materials. One promising direction is the integration of MOFs with two-dimensional materials such as graphene and MoS₂, which can enhance electrical conductivity and charge transport.

The development of Z-scheme and S-scheme heterojunction systems is another exciting area of research. These systems mimic natural photosynthesis and provide efficient charge separation pathways, leading to improved photo catalytic performance. Additionally, defect engineering and doping optimization can be used to fine-tune the electronic structure and create more active sites.

The use of artificial intelligence and machine learning for material design is also gaining attention. These tools can help predict optimal compositions and structures, accelerating the discovery of high-performance photo catalysts.

Furthermore, efforts should be focused on developing cost-effective and scalable synthesis methods to enable practical applications. With continued research and innovation, RE–TM–MOFs have the potential to play a significant role in sustainable hydrogen production.

9. Conclusion

In conclusion, rare-earth doped transition metal–organic frameworks (RE–TM–MOFs) represent a highly promising class of materials for efficient photocatalytic hydrogen evolution. The synergistic combination of rare-earth ions, transition metal centers, and organic linkers enables enhanced light absorption, efficient charge separation, and improved catalytic activity. The incorporation of advanced components such as Ru–phenanthroline complexes and plasmonic metals further boosts performance, making these systems highly effective for solar-driven hydrogen production. Despite challenges such as stability, cost, and scalability, ongoing research efforts are addressing these issues through innovative design strategies and material optimization. The future of RE–TM–MOFs lies in the development of multifunctional, stable, and cost-effective systems that can be implemented on a large scale.

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