

# The rise of single-atom catalysts in hematite photoanodes for photoelectrochemical water splitting

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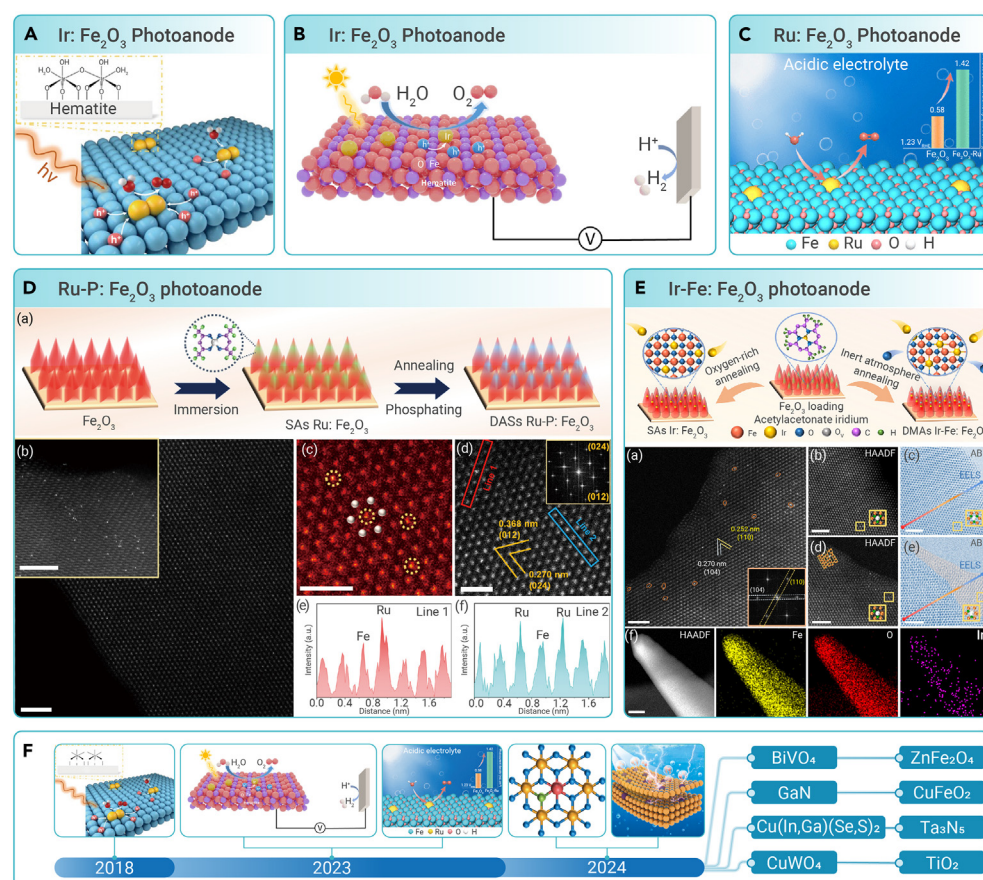
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## INTRODUCTION

The urgent imperative to achieve “carbon peak and carbon neutrality” has spurred a surge of researchers to vigorously advance the development of renewable energy technologies. Under the circumstances, there is a burgeoning interest in developing diverse solar energy utilization methods. Photoelectrochemical (PEC) water splitting, a process that harnesses sunlight, semiconductor materials, and water to transform solar energy into hydrogen energy, has emerged as a promising, environmentally friendly, and cost-effective solution. This process is frequently referred to as the “Holy Grail reaction” of solar energy utilization. Hematite-based photoanodes have attracted significant attention owing to their multitude of advantages: abundance, a suitable band gap, environmental friendliness, high photochemical stability, and exceptional theoretical solar-to-hydrogen (STH) efficiency. However, they still confront several challenges, including insufficient light absorption, limited hole diffusion length, shortened carrier lifetime, slow water oxidation reaction kinetics, and inadequate electrical conductivity. These issues result in significant electron and hole recombination within the bulk, at interfaces, and on surface regions, substantially degrading the PEC water splitting performance. Achieving rapid electron-hole separation and transport among the substrate, semiconductor, co-electrocatalyst, and electrolyte in hematite-based photoanodes is essential for attaining superior STH

conversion efficiency. Previous studies have shown that surface states mediated the charge transport process, which is crucial for understanding the PEC water splitting mechanism and enhancing the PEC water splitting performance of hematite-based photoanodes. However, the relationship between the surface/interface structure and surface states of hematite-based photoanodes, and their influence on PEC water splitting, is still not fully understood. Recently, the loading of single-atom catalysts (SACs) onto hematite photoanodes and the exploration of their reaction mechanisms have garnered significant attention from researchers.<sup>1–5</sup>

On the one hand, the investigation of SACs has rapidly developed over the past 10 years due to their facile synthesis methods, high metal utilization, and practical reliability. The synthesis methods of SACs can be classified into bottom-up approaches, such as pyrolysis routes, and top-down approaches, including mass-selected soft landing, wet deposition, impregnation, co-precipitation, physical vapor deposition, atomic layer deposition, and host engineering. Top-down approaches have recently been employed to fabricate SAC-decorated hematite photoanodes.<sup>1–3</sup> For instance, Wang et al. decorated hematite with Ir SACs via impregnation and correlated the SAC loading density with the PEC water splitting performance, revealing a close relationship between the surface Ir SAC density, hole concentration, and PEC water oxidation reaction kinetics (Figure 1A). It was



**Figure 1. The recent representative progress of single-atom catalysts in hematite photoanodes for photoelectrochemical water splitting** (A) Schematic illustration of Ir dinuclear single-atom catalysts on hematite (Ir:Fe<sub>2</sub>O<sub>3</sub>) photoelectrode. Reproduced from Liu et al.<sup>1</sup> with permission from John Wiley & Sons, copyright 2023. (B) Iridium single-atom catalysts on hematite (Ir:Fe<sub>2</sub>O<sub>3</sub>) photoanode. Reproduced from Guo et al.<sup>2</sup> with permission from American Chemical Society, copyright 2023. (C) Ru single-atom catalyst-decorated hematite (Ru:Fe<sub>2</sub>O<sub>3</sub>) photoanode. Reproduced from Li et al.<sup>3</sup> with permission from American Chemical Society, copyright 2023. (D) Ru-P:Fe<sub>2</sub>O<sub>3</sub> photoanode and the corresponding high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) characterization. Reproduced from Gao et al.<sup>4</sup> with permission from the National Academy of Sciences, copyright 2023. (E) Ir-Fe:Fe<sub>2</sub>O<sub>3</sub> photoanode and the corresponding HAADF-STEM characterization. Reproduced from Gao et al.<sup>5</sup> with permission from Elsevier, copyright 2024. (F) Development trend of single-atom catalyst-decorated photoelectrodes for photoelectrochemical water splitting.

clearly demonstrated that a low loading density of SACs on hematite photoanodes facilitated the charge transportation process under specialized PEC water oxidation conditions. Considering that sunshine intensity drops to about 0.5 kW/m<sup>2</sup> due to seasonal variations and can frequently fall to approximately 0.2 kW/m<sup>2</sup> during severe weather, a suitable SAC loading on hematite photoanodes is vital for maximizing the performance of outdoor PEC water splitting devices.<sup>1</sup> Meanwhile, Sobrido et al. explored the reaction mechanism of hematite photoanodes decorated with iridium SACs (Ir:Fe<sub>2</sub>O<sub>3</sub>) via impregnation (Figure 1B).<sup>2</sup> By combining intensity-modulated photocurrent spectroscopy (IMPS), transient absorption spectroscopy (TAS), and density functional theory (DFT) calculations, the fundamental mechanism of iridium SACs on hematite photoanodes was systematically analyzed. The iridium SACs in Ir:Fe<sub>2</sub>O<sub>3</sub> photoanodes acted as genuine catalysts, capturing holes from the bulk hematite and passing them to the electrolyte to drive the PEC water splitting reaction. Compared with pristine hematite photoanodes, Ir:Fe<sub>2</sub>O<sub>3</sub> photoanodes possess a shortened hole lifetime and a reduced hole concentration according to the TAS experiments. Meanwhile, the IMPS result revealed that Ir:Fe<sub>2</sub>O<sub>3</sub> photoanodes possess a faster surface charge transfer process than pristine hematite photoanodes. The electronic structure comparison between pristine Fe<sub>2</sub>O<sub>3</sub> and Ir:Fe<sub>2</sub>O<sub>3</sub> photoanodes via theoretical calculations indicated that the Ir 4d orbitals of iridium SACs in the Ir:Fe<sub>2</sub>O<sub>3</sub> photoanode lead to the formation of mid-gap states, facilitating hole transfer from hematite to iridium SACs. DFT calculations further evidenced that iridium SACs in Ir:Fe<sub>2</sub>O<sub>3</sub> photoanodes provided the fastest pathway for PEC water oxidation. Additionally, Gibbs free energy calculations indicated that the PEC water oxidation reaction taking place on Ir sites was more energy efficient than the Fe sites at the Ir:Fe<sub>2</sub>O<sub>3</sub> photoanode. This evidence suggests that iridium SACs function as genuine active sites, boosting the PEC water oxidation reaction rather than just prolonging the lifespan of photogenerated carriers, as in the case of the Ir:Fe<sub>2</sub>O<sub>3</sub> photoanode. This work systematically investigated the atomic structure, electronic states, and charge transportation of SACs/hematite photoanodes, providing insights into the PEC water splitting reaction mechanism.<sup>2</sup> Regarding SAC-decorated hematite photoanodes working in acidic electrolytes, Wang et al. reported the fabrication of Ru SAC-modified hematite (Ru:Fe<sub>2</sub>O<sub>3</sub>) photoanodes via impregnation method, enabling a 1.42 mA/cm<sup>2</sup> photocurrent response at 1.23 V<sub>RHE</sub> in a 0.1 M HNO<sub>3</sub> and 0.1 M NaNO<sub>3</sub> electrolyte (Figure 1C).<sup>3</sup> Comprehensive experimental and theoretical studies have revealed the detailed reaction mechanisms rationalizing the excellent PEC water oxidation activity of Ru:Fe<sub>2</sub>O<sub>3</sub> photoanodes. The presence of Ru SACs in Ru:Fe<sub>2</sub>O<sub>3</sub> photoanodes introduced additional energy levels within the hematite band gap, reducing the charge recombination and boosting the PEC water oxidation kinetics. Consequently, the modification of hematite photoanodes with Ru SACs effectively accelerated the rate-determining steps of the PEC water oxidation reaction.

On the other hand, the modification of hematite photoanodes with pair-atom catalysts opened up new horizons for the PEC water splitting community.<sup>4,5</sup> Wang et al. decorated hematite with metal-nonmetal diatomic Ru-P pair-site catalysts (Ru-P:Fe<sub>2</sub>O<sub>3</sub>) through the chemical vapor deposition method, achieving an excellent photocurrent response of 4.55 mA/cm<sup>2</sup> at 1.23 V<sub>RHE</sub> (Figure 1D).<sup>4</sup> The Ru-P chemical bonds substantially reduced the deep electron trapping sites in comparison with the Ru-O and P-O chemical bonds in the Ru-P:Fe<sub>2</sub>O<sub>3</sub> photoanode. The presence of Ru-P chemical bonds in the Ru-P:Fe<sub>2</sub>O<sub>3</sub> photoanodes also reduced the charge recombination and accelerated the charge separation and transportation, ensuring that more holes participate in the PEC water oxidation reaction. Most recently, Wang et al. reported the loading of Ir-Fe pair SACs onto hematite via impregnation method, exhibiting an excellent PEC water splitting performance of 4.4 mA/cm<sup>2</sup> at 1.23 V<sub>RHE</sub> (Figure 1E).<sup>5</sup> Through a combination of X-ray adsorption fine-structure spectroscopy, IMPS, TAS, and theoretical dynamic calculations, the authors revealed that the electron coupling effect of Ir and Fe atoms resulted in partially occupied orbitals at Ir-Fe pair SACs of the Ir-Fe:Fe<sub>2</sub>O<sub>3</sub> photoanode, thereby enabling the rapid desorption of OH\* intermediates at Ir sites. This work indicates that fabrication SACs with suitable chemical coordination onto hematite photoanodes is important for boosting PEC water splitting performance. Overall, previous investigations have revealed that the

incorporation of SACs in hematite photoanodes has a limited effect on the hole diffusion length, but it substantially increases the carrier lifetime and enhances the efficiency of charge separation and transfer. These improvements accelerate water oxidation kinetics on the surface of hematite photoanodes and thus boost its PEC water splitting performance.<sup>1–5</sup>

## CONCLUSION

Due to their unique atomic structure, atomic coordination, and tuned electronic states, SAC materials have been widely applied in heterogeneous catalysis, electrochemical catalysis, and photocatalysis systems. However, the application of SACs in PEC water splitting has been rare until recent reports on several metallic SAC-decorated hematite photoanodes for PEC water splitting. Considering the nascent nature of SAC application in hematite photoanodes, achieving a thorough understanding of their detailed PEC water splitting processes remains challenging. Given that the detailed surface/interface structures of SAC-decorated photoelectrodes and the surface states are interrelated and crucial factors for PEC water splitting performance, further rational design of photoelectrodes with SACs inevitably requires the subtle selection of SAC species and collaborative design of SACs and photoelectrode materials. Controlling atom-atom interactions between SACs and photoelectrode materials is expected to modulate the atomic structure, local coordination, and electronic states of composite photoelectrodes, thus affecting charge transfer and recombination efficiency, onset potential, photocurrent response, reaction intermediates, and reaction pathways. In order to further investigate the reaction intermediates and reaction mechanisms of SACs/photoelectrodes, we propose that more efforts should be devoted to developing *in situ* PEC techniques. In this way, experimental and theoretical data could be combined to further accelerate the development of photoelectrodes with SACs for PEC water splitting. In the near future, as shown in Figure 1F, the application of SACs is expected to extend to other photoelectrodes (including WO<sub>3</sub>, BiVO<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub>, CuWO<sub>4</sub>, GaN, CuFeO<sub>2</sub>, Ta<sub>3</sub>N<sub>5</sub>, Cu(In,Ga)(Se,S)<sub>2</sub>, etc.), further boosting the practical application of PEC water splitting systems.

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## DECLARATION OF INTERESTS

The authors declare no competing interests.