



Editorial

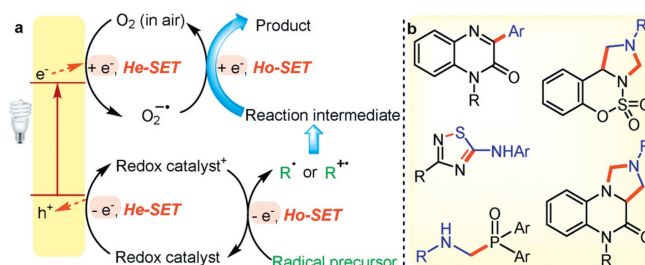
Double redox-mediated intrinsic semiconductor photocatalysis: Practical semi-heterogeneous synthesis



Photoredox catalysis has made significant advances in state-of-the-art chemical synthesis, drawing energy from inexhaustible light and enabling various organic transformations to occur under mild reaction conditions. Over the past few years, a variety of homogeneous and heterogeneous photocatalysts have been applied in the photoredox catalysis. Heterogeneous photoredox catalysis offers advantages such as easy separation and superior recyclability compared to homogeneous counterparts, although homogeneous catalysts are usually associated with higher activities and selectivity. From a practical perspective, an optimal photoredox catalytic system would integrate the advantages of both homogeneous and heterogeneous cases.

Semiconductor materials with suitable bandgaps are among the most widely studied heterogeneous photoredox catalysts due to their excellent recyclability and chemical stability [1,2]. When semiconductor materials are exposed to sufficient light energy, their electron are excited and transition from the valence band (VB) to the conduction band (CB), creating a hole (h^+)-electron (e^-) pair. This transient state can be utilized for redox events, which activate substrates through single electron transfer (SET) steps, leading to the formation of highly active radical or radical ion species. However, the practical application of low-cost, commercially available intrinsic semiconductor photocatalysts is often hampered by the fast recombination of photon-generated h^+ - e^- pair and the deactivation of the photocatalysts. Although surface modification technologies can improve their photochemical properties of semiconductors, these protocols not only involve tedious synthetic procedures but also rely on sensitive and toxic precursors, which hinder their practical application. Consequently, developing an eco-friendly and practical strategy to overcome the inherent limitations of intrinsic semiconductor photocatalysts is highly challenging and desirable.

Recently, Prof. Wei-Min He's group at University of South China developed the double redox-mediated intrinsic semiconductor photocatalysis (DRISP) systems [3–7], making an important breakthrough in semiconductor photocatalysis Scheme 1. This strategy employs a catalytic amount of low-cost and abundant redox reagent (iodide salt, ferrocene, tetramethylpiperidine *N*-oxide, etc.) as h^+ acceptors, and ambient air as the e^- acceptor, to prevent recombination. In the DRISP process, a heterogeneous single electron transfer (He-SET) process first occurs between the ground-state redox catalyst and h^+ , yielding the oxidation-state redox catalyst. This catalyst then undergoes a homogeneous SET (Ho-SET) process with the radical precursor to generate the re-



Scheme 1. Double redox-mediated intrinsic semiconductor photocatalysis.

active radical (or radical ion) intermediate and re-produces the ground-state redox catalyst. The radical intermediate subsequently triggers a bond-forming reaction to produce the reaction intermediate. Simultaneously, e^- reduces ground-state O_2 (from air) to yield the higher active excited $O_2^{\bullet -}$ via a He-SET process, which promotes the conversion of reaction intermediate into the target product and the re-generation of the ground-state O_2 via a Ho-SET process. In addition, redox catalysts are useful in mitigating intrinsic semiconductor passivation caused by the formation of polymer films on the semiconductor surface. Furthermore, the kinetic inhibition which is typically associated with the electron transfer from semiconductor to the reactant, can be eliminated. Using this strategy, He and colleagues accomplished the sustainable synthesis of a series of high value-added chemicals, including 3-arylquinoxaline-2(1*H*)-ones [3], benzoimidazothiazine 5,5-dioxides [4], imidazo[1,5-*a*]quinoxalinones [5], 5-amino-1,2,4-thiadiazoles [6], α -amino phosphine oxides [7], etc.

The DRISP strategy represents a significant development in the field of heterogeneous photocatalysis and offers an environmentally friendly, simple, and practical tool for constructing high-value-added products. By using both redox reagents and ambient air as catalyst, this system fully utilizes photo-generated electrons and holes for the bond-formation. This not only addresses the inherent limitations of intrinsic semiconductor catalysis, but also improves the catalytic efficiency of organic transformation. The key advantages of this DRISP include usage of cheap and commercially available intrinsic semiconductor photocatalysts and redox reagents, solar-driven nature, simple and mild conditions, gram scale synthesis, and excellent reusability of the photocatalyst. Considering the impressive progress achieved in homogeneous photosynthesis, and the growing pressure of the global energy crises and

environmental pollution, the development of DRISP is expected to flourish in the near future.

Declaration of interest statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRedit authorship contribution statement

Xin He: Writing – review & editing. **Feng Liu:** Writing – review & editing. **Tao Tu:** Writing – review & editing, Writing – original draft.

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