

Research Highlight

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Ultrafast S-scheme interfacial electron transport enhances CO₂ photoreduction

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The increasing gap between CO₂ emissions from human activities and the carbon capture and sequestration capabilities of natural ecosystems has intensified the focus on achieving global net-zero carbon emissions^[1-3]. Photocatalytic CO₂ reduction, which transforms CO₂ into high-value-added fuels or chemicals, presents a promising strategy for reaching carbon neutrality^[4-6]. However, challenges associated with photocatalysts, such as limitations in light absorption, rapid recombination of photogenerated carriers, and kinetic barriers, significantly hinder CO₂ photoconversion efficiency^[7]. As a result, the development of efficient photocatalysts to improve CO₂ reduction efficiency has become a key research priority in the field of photocatalysis^[8,9].

Among various photocatalyst design strategies, S-scheme heterojunctions composed of reduction and oxidation semiconductors have gained significant attention^[10,11]. Compared with single-component photocatalysts and type-II heterojunctions, S-scheme heterojunctions not only facilitate efficient separation of photogenerated carriers but also enhance redox capacity, providing a distinct advantage for CO₂ photoreduction^[12-14]. However, low-quality interfaces in these heterojunctions often impede efficient interfacial electron transport, thereby limiting overall photocatalytic efficiency.



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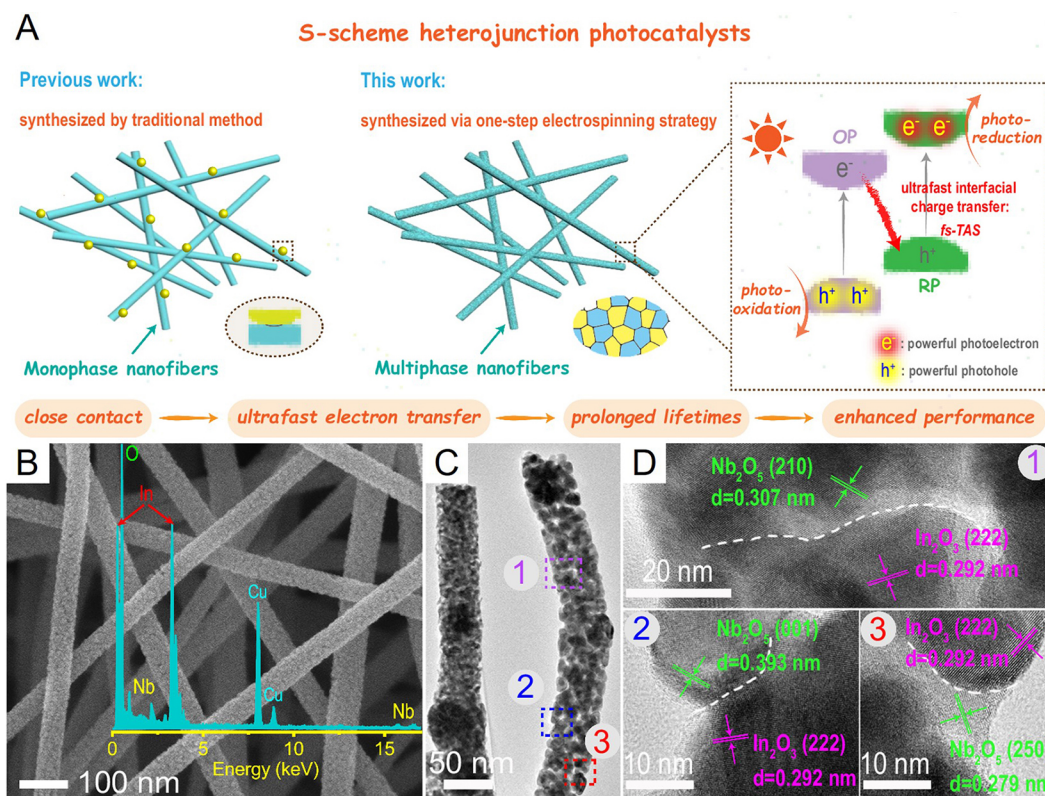


Figure 1. (A) Schematic illustration and design concept of the study; (B) Field emission scanning electron microscopy image and energy-dispersive X-ray spectrum; (C) TEM image; and (D) high-resolution TEM images of the In₂O₃/Nb₂O₅ heterojunctions (IN10). This figure is quoted with permission from Deng et al.^[15]. OP: Oxidation photocatalysts; RP: reduction photocatalysts; fs-TAS: femtosecond transient absorption spectroscopy.

To address this issue, Deng et al. recently developed an S-scheme In₂O₃/Nb₂O₅ heterojunction photocatalyst, denoted as IN_x^[15]. In this designation, “I” stands for In₂O₃, “N” represents Nb₂O₅, and “x” indicates the weight percentage of Nb₂O₅ relative to In₂O₃. This catalyst was prepared using a one-step high-temperature calcination process after electrospinning the precursor into fibers [Figure 1A]. Unlike conventional two- or multi-step synthesis strategies, this “one-pot” approach allowed for the simultaneous synthesis of In₂O₃ and Nb₂O₅, ensuring optimal contact between the two components. Transmission electron microscopy (TEM) images revealed that the close contact between In₂O₃ and Nb₂O₅ created an extensive two-phase interface, significantly enhancing carrier transport efficiency [Figure 1B–D]. This design strategy created a high-quality carrier transport channel, facilitating efficient interfacial charge transfer.

Femtosecond transient absorption spectroscopy indicated that the ground-state bleach (GSB) signal of In₂O₃ is attributed to photogenerated electrons [Figure 2], as confirmed by using AgNO₃ as an electron scavenger. In pristine In₂O₃, photogenerated electrons undergo interband diffusion and shallow trap state capture [Figure 2A and E]. However, in the S-scheme In₂O₃/Nb₂O₅ heterojunction, a new process is observed: the transfer of photogenerated electrons from the conduction band of In₂O₃ to the valence band of Nb₂O₅ [Figure 2B and F]. Under an argon atmosphere, increasing the Nb₂O₅ content in the heterojunction reduces interband diffusion and shallow trap state capture due to competition with the S-scheme interfacial electron transfer [Figure 2C]. In a CO₂ environment, the consumption of electrons by CO₂ further intensifies this competition, resulting in S-scheme electron transfer occurring in less than 10 ps [Figure 2D and G]. This rapid transfer suppresses electron recombination and significantly extends electron lifetime.

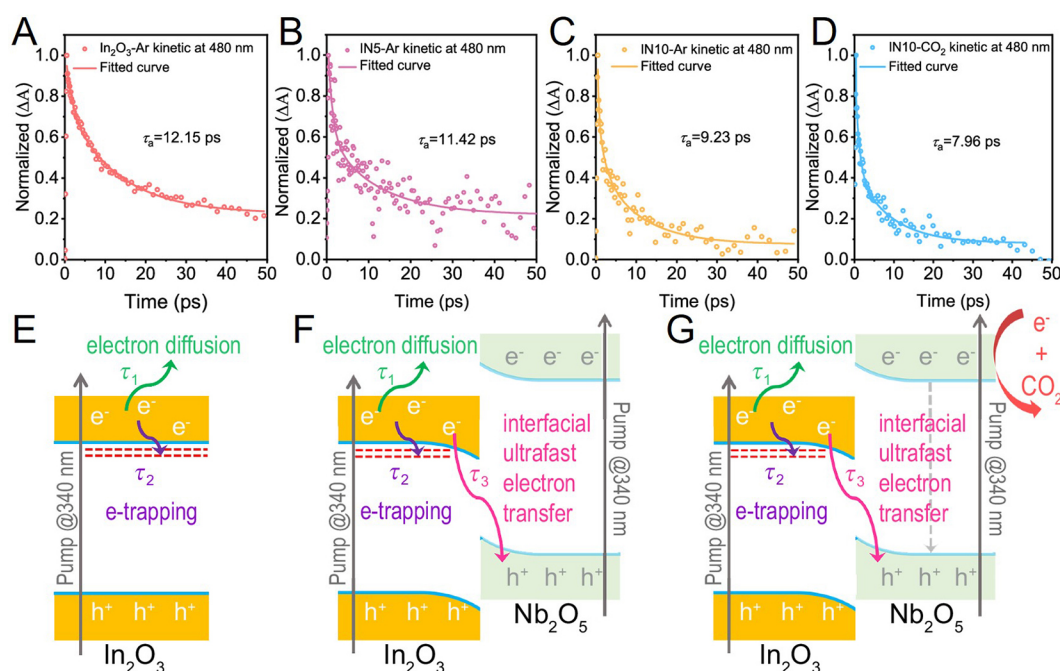


Figure 2. Charge carrier dynamic decay for (A) pure In_2O_3 in Ar; (B) IN5 in Ar; (C) IN10 in Ar; and (D) IN10 in CO_2 ; schematic illustrations of the decay pathways of photogenerated electrons in (E) pure In_2O_3 ; (F) $\text{In}_2\text{O}_3/\text{Nb}_2\text{O}_5$ heterojunctions in Ar; and (G) $\text{In}_2\text{O}_3/\text{Nb}_2\text{O}_5$ heterojunctions in CO_2 . This figure is quoted with permission from Deng et al.^[15].

In contrast, the GSB signal of Nb_2O_5 was attributed to photogenerated holes [Figure 3], as verified by using lactic acid as a hole scavenger. In Nb_2O_5 , photogenerated holes participate in recombination with both intrinsic photogenerated electrons and electrons transferred from In_2O_3 [Figure 3A and E]. Under an argon atmosphere, the half-life of photogenerated holes in Nb_2O_5 within the $\text{In}_2\text{O}_3/\text{Nb}_2\text{O}_5$ heterojunction is shorter than that in pristine Nb_2O_5 due to rapid hole consumption by ultrafast interfacial electron transfer [Figure 3B and F]. When Nb_2O_5 content is excessive, In_2O_3 photogenerated electrons cannot fully consume the Nb_2O_5 photogenerated holes, resulting in an extended hole lifetime [Figure 3C]. In a CO_2 atmosphere, although CO_2 reacts with photogenerated electrons, reducing hole consumption, it also accelerates the transfer of electrons from In_2O_3 to the valence band of Nb_2O_5 and increases hole recombination. Thus, the lifetime of photogenerated holes in the heterojunction does not significantly differ between CO_2 and argon atmospheres [Figure 3D and G].

Photocatalytic CO_2 reduction experiments demonstrated that the primary product across all samples was CO, exhibiting nearly 100% selectivity [Figure 4A]. Pure In_2O_3 and Nb_2O_5 displayed poor photocatalytic performance due to the rapid recombination of photogenerated carriers inherent to single-phase photocatalysts. However, the formation of S-scheme heterojunctions significantly enhanced CO yield, achieving a maximum CO_2 -to-CO conversion activity of $0.21 \text{ mmol} \cdot \text{g}_{\text{active sites}}^{-1} \cdot \text{h}^{-1}$ for IN10. Furthermore, the significance of close interfacial contact between the two phases in promoting ultrafast interfacial electron transfer within the S-scheme heterojunction was validated by comparing the CO_2 photoreduction activities of IN10, $\text{In}_2\text{O}_3/\text{Nb}_2\text{O}_5$ nanohybrids synthesized via the conventional impregnation-calcination method, and physical mixtures of In_2O_3 and Nb_2O_5 [Figure 4B]. Additionally, isotopically labeled experiments revealed three mass spectral signals at $m/z = 13$, 16, and 29, corresponding to the fragments of ^{13}C , O, and ^{13}CO , respectively [Figure 4C]. These findings confirm the absence of interference from exogenous carbon sources in the origin of the products.

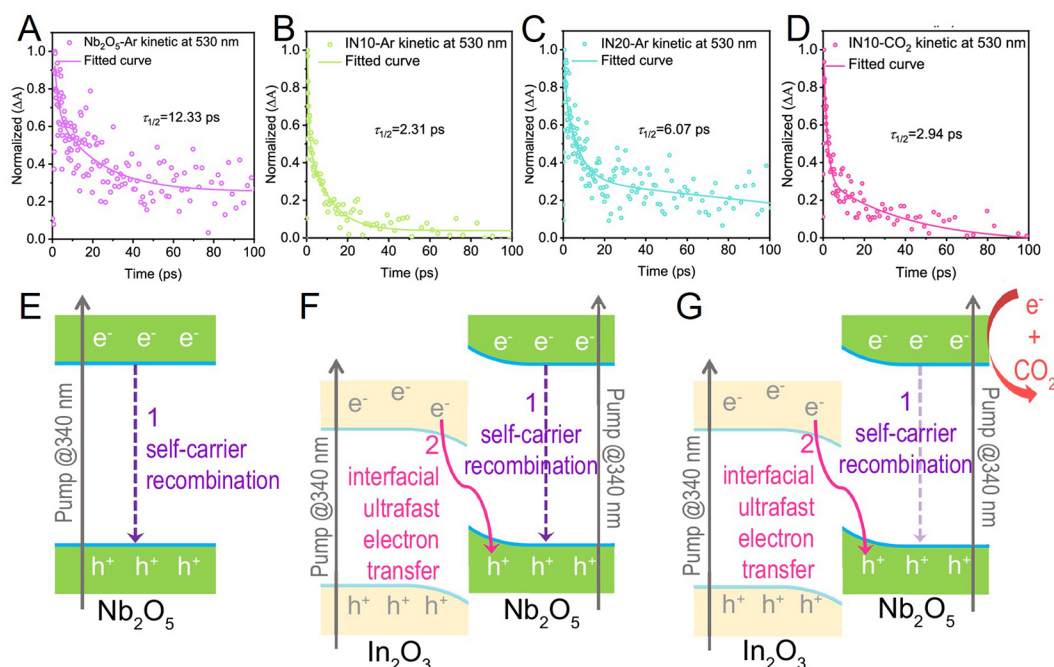


Figure 3. Charge carrier dynamic decay for (A) pure Nb₂O₅ in Ar; (B) IN20 in Ar; (C) IN10 in Ar; and (D) IN10 in CO₂; schematic illustrations of the decay pathways of photogenerated holes in (E) pure Nb₂O₅; (F) In₂O₃/Nb₂O₅ heterojunctions in Ar; and (G) In₂O₃/Nb₂O₅ heterojunctions in CO₂. This figure is quoted with permission from Deng et al.^[15]

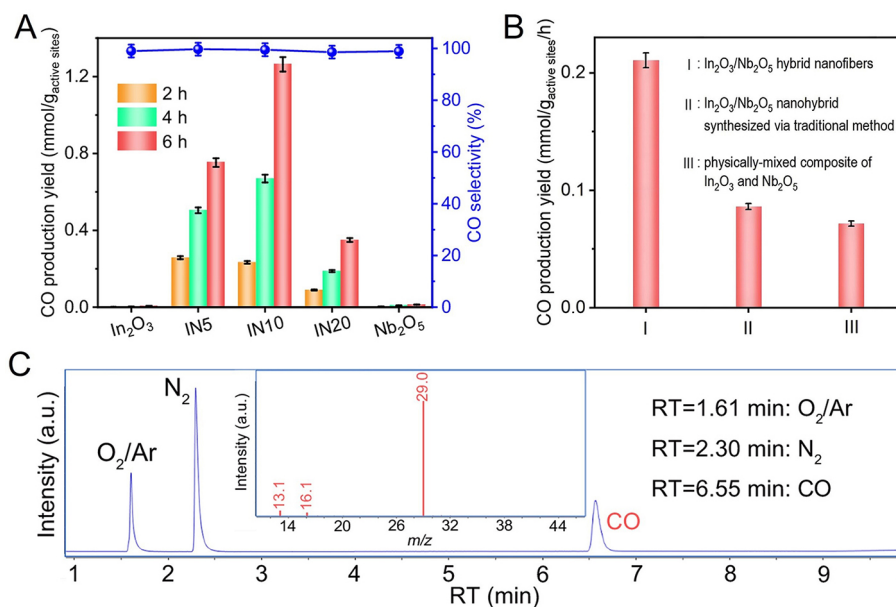


Figure 4. (A) Production yields and CO selectivity over In₂O₃, INx, and Nb₂O₅; (B) Comparison of CO₂ photoreduction performance among various In₂O₃/Nb₂O₅ composites; (C) Total ion chromatography and corresponding mass spectra of products from the photocatalytic reduction of ¹³CO₂ over IN10. RT denotes retention time. This figure is quoted with permission from Deng et al.^[15]

In summary, this work has significantly enhanced CO₂ photoreduction efficiency by developing an S-scheme In₂O₃/Nb₂O₅ heterojunction photocatalyst with high-quality interfacial transport channels. It underscores the critical role of high-quality heterojunction interfaces in achieving ultrafast carrier transport

and provides valuable insights for the design of future heterojunction photocatalysts.

DECLARATIONS

Authors' contributions

Wrote the draft manuscript: Yang J

Revised and rewrote the manuscript: Bie C

Availability of data and materials

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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