Molecular co-catalyst accelerating hole transfer for enhanced photocatalytic $\text{H}_2$ evolution

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In artificial photocatalysis, sluggish kinetics of hole transfer and the resulting high-charge recombination rate have been the Achilles' heel of photocatalytic conversion efficiency. Here we demonstrate water-soluble molecules as co-catalysts to accelerate hole transfer for improved photocatalytic $\text{H}_2$ evolution activity. Trifluoroacetic acid (TFA), by virtue of its reversible redox couple $\text{TFA}^+/\text{TFA}^-$, serves as a homogeneous co-catalyst that not only maximizes the contact areas between co-catalysts and reactants but also greatly promotes hole transfer. Thus $\text{K}_4\text{Nb}_6\text{O}_{17}$ nanosheet catalysts achieve drastically increased photocatalytic $\text{H}_2$ production rate in the presence of TFA, up to 32 times with respect to the blank experiment. The molecular co-catalyst represents a new, simple and highly effective approach to suppress recombination of photogenerated charges, and has provided fertile new ground for creating high-efficiency photosynthesis systems, avoiding use of noble-metal co-catalysts.
Photocatalytic conversion of solar energy to fuels is considered to be an ideal, renewable energy resource for the future, yet the relatively low-energy conversion efficiency remains the most critical factor that limits its practical applications. In principle, the generation of electron–hole pairs in photocatalysts upon illumination and their participation in subsequent redox reactions are the main processes among the widely investigated photocatalytic reactions. To achieve highly efficient photochemical conversion, the main challenge in photocatalysis is to maximize the extraction of charge carriers while suppressing their recombination. Arguably, the electron transfer is typically sufficiently fast, whereas the transport of hole and subsequent reactions are generally slow, eventually leading to the high-charge recombination rate. From this perspective, accelerating hole transfer kinetics, typically the rate-limiting step, has emerged as the inevitable route to achieve high-efficiency charge separation.

Co-catalysts are known to provide trapping sites for the photogenerated charges and promote charge separation. Noble-metal oxides (such as RuO$_2$ and IrO$_2$) are usually used as co-catalysts for hole transport because they can effectively lower the overpotential for the oxidation reaction. Meanwhile, subjected to their high costs of upscaling, several cost-effective and earth-abundant alternatives (primarily based on Co-Pi, NiO$_2$, and so on) have also been exploited and achieve relatively high efficiency. However, this strategy through solid-state co-catalysts loading is potentially limited by finite contact areas between co-catalysts and reactants, lacking sufficient active sites for catalysis.

Alternatively, homogeneous catalysis, free from limited contact areas, has gained considerable attention due to its high activity and selectivity. For example, biological hydrogenases and redox enzymes, has gained considerable attention due to its high activity for catalysis.

**Results**

**K$_4$Nb$_6$O$_{17}$ nanosheets.** Layered niobate is a well-accepted photocatalytic system for water splitting, and its unique layered structure has boosted new opportunities for the manipulation of two-dimensional nanomaterials by intercalation and delamination. Benefiting from the highly anisotropic structure, niobate ultrathin nanosheets allow advances in potentially exposing more reactive sites and facilitating the contact of catalysts with reactants, and thus provide an ideal platform for artificial photocatalysis. Here K$_4$Nb$_6$O$_{17}$ nanosheet catalysts were synthesized via a conventional solution method by anisotropic growth. The as-synthesized K$_4$Nb$_6$O$_{17}$ catalysts showed a typical nanosheet morphology with lateral size varied from 100 to 500 nm, as shown by scanning electron microscopy (SEM) and transmission electron microscopy (TEM; Supplementary Fig. 1). In addition, the well-resolved lattice features in high-resolution transmission electron microscope (HRTEM) image revealed the high crystallinity of these nanosheets and the interplanar distances coincided well with that of (200) and (002) facets respectively.

**Photocatalytic performance.** As illustrated in Fig. 1, the reversible redox couple TFA$^+$/$\text{TFA}^-$ and the highly active intermolecular radical reactions make TFA molecule a robust hole shuttle, effectively promoting the charge separation of K$_4$Nb$_6$O$_{17}$ catalysts, and thus leading to improved photocatalytic activity. Figure 2a shows the comparison of H$_2$ evolution rates on K$_4$Nb$_6$O$_{17}$ nanosheet catalysts with extra addition of different amounts of TFA as molecular co-catalyst. K$_4$Nb$_6$O$_{17}$ nanosheets alone showed low activity in photocatalytic H$_2$ evolution (ca.195 μmol g$^{-1}$ h$^{-1}$). Notably, when TFA as co-catalyst was added, the H$_2$ evolution activity turned out to be dramatically
enhanced. Substantial increase of H₂ evolution rates was observed with the molar ratio of TFA/K₄Nb₆O₁₇ ranging from 2.56 to 25.6, reaching a maximum value of 6.344 μmol g⁻¹ h⁻¹, up to 32 times with respect to that of bare K₄Nb₆O₁₇ nanosheets without TFA. Notably, increasing the molar ratio of TFA/K₄Nb₆O₁₇ above 25.6 did not bring about further obvious increase for photocatalytic performance which is probably due to the saturated adsorption of TFA molecules on the surface of K₄Nb₆O₁₇ catalysts, as confirmed by elemental analysis in Supplementary Table 1 and Supplementary Note 1. In a word, niobate photocatalyst achieved a significantly improved H₂ generation rate when water-soluble TFA molecule was used as co-catalyst.

Recycling test of photocatalytic H₂ evolution on the K₄Nb₆O₁₇ nanosheet catalysts with addition of 100 μl TFA was performed to evaluate the photocatalytic stability during a long-term photocatalytic reaction. As shown in Fig. 2b, the respective total amount of H₂ after 20h illumination was 6.344 mmol and no noticeable degradation was detected during the four consecutive reactions, which indicates the high stability of K₄Nb₆O₁₇ catalysts and that no obvious side reactions associated with TFA consumption occurred during the photocatalytic process. The reversibility of TFA was further verified by 19F NMR. As illustrated in Supplementary Fig. 2 and Supplementary Note 2, no new fluoride species were detected after the reaction. And according to the quantitative characterization results, the concentration of TFA remains constant during the whole photocatalytic process.

To disclose the role of TFA molecules in the photocatalytic H₂ evolution reaction, a series of control experiments were carried out for comparison. Control experiment without methanol but with only 100 μl TFA (Supplementary Fig. 3a) showed a relatively low activity in photocatalytic H₂ evolution (ca. 158 μmol g⁻¹ h⁻¹), indicating a synergistic effect exists between TFA molecules and CH₃OH. Meanwhile, to rule out the influence from the changes of hydrogen ion concentration whose relaxation can be characterized by two time constants and optical properties of the K₄Nb₆O₁₇ nanosheets with/without addition of TFA after the catalytic reaction. SEM and TEM images in Supplementary Fig. 1 revealed that K₄Nb₆O₁₇ catalysts still kept the initial nanosheet morphology after reaction. X-ray powder diffraction and HRTEM further confirmed structural maintenance. High-resolution X-ray photoelectron spectroscopy analysis of the K₄Nb₆O₁₇ nanosheet catalysts after TFA addition (Supplementary Fig. 4a) showed an additional peak at 688.6 eV corresponding to a bandgap of 688.6 eV which can be attributed to the -CF₃ groups, indicating the preferential adsorption of TFA on the surface of K₄Nb₆O₁₇ nanosheets. The optical properties were measured using ultraviolet–visible absorption spectra in the wavelength range of 220–800 nm (Supplementary Fig. 4b). The absorption edge of K₄Nb₆O₁₇ nanosheet catalysts was observed at ~348 nm, corresponding to a bandgap of 3.56 eV. Upon TFA addition, a weak absorption enhancement in the ultraviolet region was observed, which probably originates from the absorption of TFA itself, whereas the absorption edge of photocatalysts showed no noticeable shift. This result demonstrates that the improved photocatalytic performance cannot be ascribed to the enhancement of light absorption, but instead to the effective charge separation. 

TA and PL analyses. To evaluate how the addition of TFA affects the charge separation behaviour involved in the K₄Nb₆O₁₇ nanosheet catalysts, we interrogated the K₄Nb₆O₁₇ and K₄Nb₆O₁₇–TFA samples by means of ultrafast transient absorption (TA) spectroscopy, which is known as a robust tool for tracking in real-time charge carrier dynamics in nanosystems. In our TA measurements, a femtosecond ultraviolet pump/white-light continuum probe scheme was employed (see Supplementary Methods for details of the pump–probe experiments). The centre wavelength of the pump pulses was chosen at 300 nm, which can effectively photo-induce an interband transition in the semiconductor K₄Nb₆O₁₇ system (refer to Supplementary Fig. 4b). Since the 390 – 610 nm white-light continuum probe was found to yield essentially the same TA kinetics for each sample, we show here a set of representative data taken at 500 nm (Fig. 3a,b). It turned out that both samples exhibited TA signals due to photoinduced absorption, whose relaxation can be characterized by two time constants: τ₁ = 7 ± 1 ps and τ₂ = 219 ± 18 ps for K₄Nb₆O₁₇ while τ₁ = 10 ± 2 ps and τ₂ = 522 ± 62 ps for K₄Nb₆O₁₇–TFA (all with a roughly 40:60 percentage for the two exponential components). Note that the long-time decay component(s) cannot be identified.
Figure 3 | Spectroscopic evidence for effective charge separation process. Representative ultrafast TA kinetics probed at 500 nm (pump at 300 nm) for K$_4$Nb$_6$O$_{17}$ nanosheets in the (a) absence and (b) presence of TFA. The TA signal (that is, the absorbance changes, or $\Delta$Abs. in short) is given in mOD where OD stands for optical density. (c) PL emission and (d) time-resolved PL spectra (excitation at 315 nm, emission at 430 nm) for both K$_4$Nb$_6$O$_{17}$ and K$_4$Nb$_6$O$_{17}$-TFA. (e) Schematic illustration of the mechanisms involved; see text for details.

due to the probe-delay limit of our pump–probe spectrometer (ca. 2 ns). The observed two components in the picosecond domain may reflect the electron dynamics associated with the defect states that are energetically located within the bandgap. Considering that such defect states could be long-lived (in the nanosecond domain), we resorted to photoluminescence (PL) spectroscopy. It is clearly seen from the PL spectra excited at 315 nm (Fig. 3c) that the addition of TFA results in substantial PL quenching, indicating greatly suppressed radiative electron–hole recombination in K$_4$Nb$_6$O$_{17}$–TFA with respect to K$_4$Nb$_6$O$_{17}$. Figure 3d compares the PL lifetimes recorded for the two samples at the emission wavelength of 430 nm (that is, the PL intensity maximum in Fig. 3c). Notably, two lifetimes with sizable components, as in the TA kinetics measurements, were observed for both samples: $\tau_1 = 1.45 \pm 0.04$ ns (81%) and $\tau_2 = 10.0 \pm 0.5$ ns (19%) for K$_4$Nb$_6$O$_{17}$ while $\tau_1 = 4.9 \pm 0.1$ ns (87%) and $\tau_2 = 30 \pm 2$ ns (13%) for K$_4$Nb$_6$O$_{17}$-TFA.

On the basis of the combined TA and PL observations, we illustrate in Fig. 3e the schematic mechanisms underlying the photoexcited carrier dynamics involved in the system. The observed PL emissions peaking at ca. 430 nm (that is, 2.88 eV, red-shifted with respect to the 3.56-eV bandgap) with two PL lifetimes suggest that the radiative electron–hole recombination responsible for PL could originate from two interfacial defect states (probably with different trap depths) near the conduction band (CB) bottom (labelled e-DS as a whole in Fig. 3e) that act as electron scavengers. The addition of TFA can be expected to accelerate the subsequent hole transfer from h-DS to hole scavengers in the solution (including methanol as well as TFA itself). This is understandable because the situation of h-DS being effectively vacated via the TFA anion-accelerated hole transfer will eventually decelerate the processes of electron–hole recombination and electron transfer from CB to e-DS, as verified by our observed, significantly altered carrier dynamics. It is worth stressing here that, in the presence of TFA, the average time describing the overall electron transfer from CB to e-DS is increased by a factor of ca. 2.48 (312 ± 37 ps for K$_4$Nb$_6$O$_{17}$–TFA versus 126 ± 11 ps for K$_4$Nb$_6$O$_{17}$) and

\[
\begin{align*}
\tau_1 &= 4.9 \pm 0.1 \text{ ns (87\%) for K}_4\text{Nb}_6\text{O}_{17} \\
\tau_2 &= 30 \pm 2 \text{ ns (13\%) for K}_4\text{Nb}_6\text{O}_{17}-\text{TFA}
\end{align*}
\]
Meanwhile that describing the overall radiative e–h recombination by a factor of ca. 2.73 (8.2 ± 0.4 ns for K₄Nb₆O₁₇–TFA versus 3.0 ± 0.1 ns for K₄Nb₆O₁₇). Based on the self-consistent results of PL and TA observations (see insets in Fig. 3 for details), it is understandable that TFA mainly influences the hole transport process. And it can be safely inferred that the increased electron lifetimes in the system could offer more opportunities for photogenerated electrons to participate in the H⁺ reduction reaction.

**In situ ESR characterizations.** To better understand the photocatalytic process of H₂ production in the presence of TFA, ESR technique using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a trapping regent was used to in situ monitor the intermediates. Under ultraviolet irradiation, the typical ESR spectrum of the catalysts aqueous suspensions containing only TFA is presented in Fig. 4a, which is composed of 10 lines with hyperfine constants aN = 15.5 G, aHβ = 18 G, and aF = 3.6 G. These parameters exactly match the simulated ESR spectrum of DMPO–CF₃COO adducts. Control experiments in Supplementary Fig. 5 and Supplementary Note 3 also confirmed that DMPO–CF₃COO trapping regent was used to monitor the intermediates. In situ ESR characterizations of the radicals using DMPO as the spin trapping agent (a) in K₄Nb₆O₁₇ aqueous suspensions with addition of TFA; (b) in K₄Nb₆O₁₇ aqueous suspensions with the presence of methanol, or methanol and TFA.

**Discussion**

Energy-level alignment illustrated in Fig. 5 provides further theoretical evidence for the above photocatalytic mechanism. According to the previous reports, the flat-band potential is located just below the bottom of CB for an n-type semiconductor. Thus the CB potential of K₄Nb₆O₁₇ is estimated to be −0.52 V (versus normal hydrogen electrode (NHE), pH ~7, Supplementary Fig. 6), in agreement with the previous report. Given the bandgap of 3.56 eV, the VB maximum is located at 3.04 V, which is below the potential E(TFA+/TFA⁻) = 1.90 V (Supplementary Methods) at pH = 7. Therefore, the holes in K₄Nb₆O₁₇ interfaces are able to readily react with the adsorbed TFA anions to yield TFA radicals, confirming the feasibility of TFA radicals as reactive intermediates. Meanwhile, the oxidation potential of CH₃OH is −0.39 V (versus NHE, pH ~7), is well above E(TFA+/TFA⁻). As such, CH₃OH can provide electrons to reduce the highly reactive TFA radicals. In this regard, TFA molecules stand out as recyclable co-catalysts for facilitating hole transport. Given the additional charge separation pathway across the solid–liquid interface and the extremely rapid intermolecular radical reactions, charge recombination can be effectively eliminated by a factor of ca. 2.73 (8.2 ± 0.4 ns for K₄Nb₆O₁₇–TFA versus 3.0 ± 0.1 ns for K₄Nb₆O₁₇). Based on the self-consistent results of PL and TA observations (see insets in Fig. 3 for details), it is understandable that TFA mainly influences the hole transport process. And it can be safely inferred that the increased electron lifetimes in the system could offer more opportunities for photogenerated electrons to participate in the H⁺ reduction reaction.

**Figure 4 | In situ ESR on intermediates.** ESR spectra of the radicals using DMPO as the spin trapping agent (a) in K₄Nb₆O₁₇ aqueous suspensions with addition of TFA; (b) in K₄Nb₆O₁₇ aqueous suspensions with the presence of methanol, or methanol and TFA.

**Figure 5 | Theoretical analysis for the molecular co-catalyst strategy.** Schematic illustration of the energy diagram for the K₄Nb₆O₁₇ nanosheet catalysts and the redox potentials of TFA and CH₃OH. NHE, normal hydrogen electrode.
suppressed, and therefore more electrons can be released for water reduction. On the other hand, loading Pt co-catalysts can further optimize the photocatalytic performance by promoting proton reduction reaction. As shown in Supplementary Fig. 7, the photocatalytic H₂ generation rate of Pt/K₄Nb₆O₁₇ with the addition of TFA reached 9.116 μmol g⁻¹ h⁻¹, up to 46 times with respect to that of bare K₄Nb₆O₁₇. Moreover, as in the aforementioned comparison of the self-consistent TA and time-resolved PL results of K₄Nb₆O₁₇ and K₄Nb₆O₁₇-TFA, the similar comparison of Pt/K₄Nb₆O₁₇ and Pt/K₄Nb₆O₁₇-TFA (Supplementary Fig. 8 and Supplementary Note 4) further confirms that TFA mainly influences the hole transfer process. Besides, it is worth mentioning that the enhanced hole transport with TFA is applicable to other metal oxide photocatalysts. Taking layered titanate Na₂Ti₃O₇ as an example, photocatalytic experiments confirmed the enhanced H₂ evolution activity with the addition of TFA, which is shown in Supplementary Figs 9,10.

To disclose the essentials of molecular co-catalysts, acetic acid and oxalic acid were also investigated. As shown in Fig. 6a, they also led to improved H₂ production performance in the first 4 h, 15 and 12 times higher than that of bare K₄Nb₆O₁₇ nanosheet catalysts, respectively. However, according to the ¹H NMR in Supplementary Fig. 11 and precipitation titration results in Supplementary Note 5, both acetic acid and oxalic acid underwent irreversible oxidation, which caused obvious decrease of H₂ generation rate in the long-time photocatalytic experiment shown in Fig. 6b. These results demonstrate that the reversibility needs to be taken into account when designing molecular co-catalysts.

In conclusion, we have proposed an efficient molecular co-catalyst strategy to accelerate hole transfer kinetics while suppressing charge recombination. Benefiting from the reversible redox couple TFA●/TFA and rapid intermolecular radical reactions, TFA molecule stands out as a homogenous molecular co-catalyst, leading to a roughly two-fold increase of photoexcited-electron lifetime in niobate nanosheet photocatalytic system, thus eventually leading to a dramatically improved H₂ generation rate of 6.344 μmol g⁻¹ h⁻¹, up to 32 times of that without the molecular co-catalyst. Altogether, the molecular co-catalyst strategy developed in this work provides a rational and cost-effective way for efficient separation of photogenerated charges, and hence paves a brand new avenue for designing high-efficiency photocatalytic reactions.

Methods

Synthesis of K₄Nb₆O₁₇ catalysts. K₄Nb₆O₁₇ nanosheet catalysts were synthesized via a conventional solution method with slight modification. In a typical experiment, 0.8 g Nb₂O₅ powder was added into 30 ml KOH solution (1 M). After vigorous stirring for 30 min, the mixture was transferred into a 45 ml Teflon-lined autoclave, sealed and heated at 220°C for 12–24 h. The autoclave was then allowed to cool down to room temperature naturally. The final product was washed with distilled water and ethanol alternately for several times, and then the final product was dried in vacuum at 60 °C overnight without further treatment.

Characterization methods. The samples were characterized by X-ray powder diffraction by a Philips X’Pert Pro Super diffractometer equipped with graphite-monochromatized Cu-Kα radiation (λ = 1.54178 Å). SEM images were performed on a Zeiss Supra 40 field-emission scanning microscope. TEM images were taken on H-7650 (Hitachi, Japan) operating at an acceleration voltage of 100 kV. HRTEM images were obtained on JEMOL-2010 operating at an accelerating voltage of 200 kV. The steady-state ultraviolet–visible absorption spectra were recorded on a Perkin Elmer Lambda 950 spectrophotometer. High-resolution X-ray photoelectron spectroscopy measurements were performed on a VG ESCALAB MK II X-ray photoelectron spectrometer with an excitation source of Mg Kα at 1253.6 eV. Mott-Schottky plot was measured in degassed 0.5 M Na₂SO₄ solution (pH = 6.6) at a frequency of 10 Hz in the dark and the applied potential ranges from –0.5 to +0.5 V.

TA spectroscopy characterizations. The ultrafast TA measurements were carried out on a modified Exciprobe pump–probe spectrometer (CDP) in combination with an amplified femtosecond laser system (Coherent). All the measurements were performed under ambient conditions. The samples under investigation were the K₄Nb₆O₁₇ film immersed in a methanol/water (1:4 vol%) mixed solution and the K₄Nb₆O₁₇ film immersed in a methanol/water (1:4 vol%) mixed solution with a tiny amount of TFA addition (0.5 ml l⁻¹). The sample cell was mounted on a rotating stage to ensure that the photoexcited volume of the sample was kept fresh during the course of the measurements. Detailed procedures for the femtosecond pump–probe experiments can be found in the Supplementary Methods.

PL and ESR characterizations. The PL emission spectra were obtained on a FLUOROLOG-3-TAU fluorescence spectrometer (Horiba) upon excitation at 315 nm. The ns-domain time-resolved PL spectra (excited at 315 nm; monitored at 430 nm emission) were recorded on an FL6920 fluorescence spectrometer (Edinburgh). The spin trapping experiments were performed in deoxygenated solutions using a JES-FA200 ESR spectrometer at room temperature. The irradiation experiments were carried out with a Xe lamp (500 W, USHIO Optical Module SX-U1501XQ).

Photocatalytic H₂ evolution measurements. Photocatalytic H₂ evolution reactions were carried out in a gas-closed circulation system equipped with a vacuum line. Typically, 50 mg photocatalyst powder was dispersed in 200 ml 20 vol% CH₃OH aqueous solution and then illuminated with a 300 W Xe lamp (PLS-SXE300/300UV, Trustech Co., Ltd). The amount of H₂ evolution was determined using a gas chromatography (Agilent 7890A).

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Author contributions
C.W. conceived the idea and supervised the project. W.B., X.L. and T.J. carried out the sample synthesis, characterizations and photocatalysis measurements. L.Z. and Q.Z. performed the ultrafast TA measurements. Q.Z., Y.L. and L.Z. analysed the TA and PL data. I.Z. performed the theoretical calculations. W.B., Q.Z. and C.W. cowrote the paper. Y.X. supervised the project. All the authors discussed the results and commented on the manuscript.

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