Self-cycled photo-Fenton-like system based on an artificial leaf with a solar-to-H$_2$O$_2$ conversion efficiency of 1.46%

Chaoran Dong$^1$, Yilong Yang$^1$, Xuemin Hu$^1$, Yoonjun Cho$^2$, Gyuyong Jang$^2$, Yanhui Ao$^3$$^*$$^, Luyang Wang$^4$, Jinyou Shen$^5$, Jong Hyeok Park$^2$ & Kan Zhang$^1$

Millions of families around the world remain vulnerable to water scarcity and have no access to drinking water. Advanced oxidation processes (AOPs) are an effective way towards water purification with qualified reactive oxygen species (ROSs) while are impeded by the high-cost and tedious process in either input of consumable reagent, production of ROSs, and the pre-treatment of supporting electrolyte. Herein, we couple solar light-assisted H$_2$O$_2$ production from water and photo-Fenton-like reactions into a self-cyclable system by using an artificial leaf, achieving an unassisted H$_2$O$_2$ production rate of 0.77 μmol/(min·cm$^2$) under 1 Sun AM 1.5 illumination. Furthermore, a large (70 cm$^2$) artificial leaf was used for an unassisted solar-driven bicarbonate-activated hydrogen peroxide (BAP) system with recycled catalysts for real-time wastewater purification with requirements for only water, oxygen and sunlight. This demonstration highlights the feasibility and scalability of photoelectrochemical technology for decentralized environmental governance applications from laboratory benchtops to industry.

Advanced oxidation processes (AOPs) are a recognized approach that can effectively treat various organic pollutions in aqueous solutions because the generated reactive oxygen species (ROSs) have strong oxidation capabilities for mineralizing the organic molecules$^1$. Fenton reaction is one of the most representative AOPs which can rapidly generate hydroxyl radicals (·OH) with high concentration, therefore being widely adopted in wastewater treatment engineering$^7$. However, the Fenton reaction is an irreversible process that needs the continuous supply of various chemical reagents, such as H$_2$O$_2$, iron salt, acid/alkali et al., which increases the costs of the whole wastewater treatment process by more than one time$^1$. Heterogeneous photocatalysis over semiconductors can generate a range of ROSs by photoinduced redox processes, which are regarded as green and sustainable AOPs with affordable cost$^5$. In the past several decades, numerous efforts have been devoted to photocatalytic degradation of organic pollution by developing or designing various photocatalysts and photocatalytic systems$^{1,14}$. However, directly generating ROSs by photoinduced redox processes in aqueous solutions are profoundly restricted by rapid recombination of photoinduced electron/hole pairs, and high thermodynamic barriers of radical generation (e.g., ·O$_2$ at $-0.33$ V and ·OH at $1.99$ V vs. normal hydrogen electrode, NHE), while combined photocatalysis with Fenton reaction, so-called photo-Fenton reaction, also requires the supply of H$_2$O$_2$$^6$. Therefore, there is a great necessity to find indeed efficient, low-cost, and sustainable AOPs.

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$^1$MIIT Key Laboratory of Advanced Display Material and Devices, School of Materials Science and Engineering, Nanjing University of Science and Technology, 210094 Nanjing, China. $^2$Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea. $^3$Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes of Ministry of Education, College of Environment, Hohai University, 210098 Nanjing, China. $^4$College of New Materials and New Energies, Shenzhen Technology University, Shenzhen, Guangdong, P. R. China. $^5$Jiangsu Key Laboratory of Chemical Pollution Control and Resources Reuse, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, 210094 Nanjing, China. $^*$e-mail: andyao@hhu.edu.cn; lutts@yonsei.ac.kr; zhangkan@njjust.edu.cn
In recent years, it is found that bicarbonate (HCO$_3^-$) can not only react with H$_2$O$_2$ to form HCO$_3^-$ with high reactivity but also act as an auxiliary for water-oxidative H$_2$O$_2$ evolution under photoelectrochemical (PEC) condition, through a reversible reaction as follows:\(^9\),\(^10\):

$$\text{HCO}_3^- + \text{H}_2\text{O}_2 \leftrightarrow \text{HCO}_4^- + \text{H}_2\text{O} \quad (I)$$

The above reversible reaction offers a possibility of an in situ generation and decomposition of H$_2$O$_2$ in an aqueous solution containing HCO$_3^-$ under solar light illumination\(^11\). In addition, the co-existence of HCO$_3^-$ and H$_2$O$_2$ was reported to facilitate the formation of various ROSs (O$_2$, -OH, CO$_2^-$ et al.) by Cu, Co or Mn ion activation\(^12\).\(^13\). The correlation between HCO$_3^-$, H$_2$O$_2$, HCO$_3^-$ and free radical species inspire us to design a self-cycled AOPs system with high efficiency and affordable cost\(^10\).\(^13\).

Herein, we propose a self-cycled Fenton-like system based on the deliberately designed artificial leaf, realizing the sustainable reaction system for wastewater treatment (Fig. 1a). First, the solar-motivated unassisted artificial leaf comprised of a SnO$_2$-x/BiVO$_4$/WO$_3$ photoanode and a poly tetrafluoroethylene (PTFE)-modified Mo single-atom catalysts/mildly reduced graphene oxide-coated gas diffusion electrode (PTFE@Mo-SACs/mrG-GDE) cathode fulfills the efficient H$_2$O$_2$ production in a bicarbonate-containing electrolyte with a production rate of 0.77 μmol/(min cm$^2$) under AM 1.5 G illumination, corresponding to a bias-free solar-to-hydrogen-peroxide efficiency (ShyE) of 1.46%. Second, the generated H$_2$O$_2$ can be immediately in situ activated into main ·OH, ·O$_2$ and ·O$_2$ by et al. via the catalysis of Mn(II) species in the bicarbonate electrolyte, and the Mn(II) species are correspondingly oxidized to high-valent Mn(IV) species. Third, the Mn species can be recycled by reducing the Mn(IV) species into Mn(II) in the cathode (Fig. 1a). As a result, the self-cycling process with requirements for only water, oxygen, and sunlight demonstrates long-term stability for more than one month for the removal of various organic pollutants.

**Results**

To demonstrate the self-cycled AOPs, the formation of ROSs and redox coupling of Mn(II)/Mn(IV) are first evidenced. As shown in Supplementary Fig. 1, the electron paramagnetic resonance (EPR) spectra of the co-existence of HCO$_3^-$, H$_2$O$_2$, and Mn(II) demonstrate the remarkably enhanced signal intensities of ·OH, ·O$_2$ and ·O$_2$ compared to those of the HCO$_3^-$/H$_2$O$_2$ or HCO$_3^-$/Mn(II), indicating that multi-species of ROSs can be activated by the self-cycled AOPs system\(^9\). Then, both cyclic voltammetry (CV) tests and EPR spectroscopy were used to track the Mn species. As shown in Supplementary Fig. 2, electrochemical redox peaks relative to Mn(II)/Mn(III) and Mn(III)/Mn(IV) appear in the potential window between 0.98 and 1.58 V vs. reversible hydrogen electrode (RHE), the narrower potential window would be easily met by photoinduced charge. Further insight into the valence alternation of Mn species during the redox is revealed by EPR measurement. As shown in Fig. 1b, a typical Mn(II) signal with a signature six-line pattern centered around g = 2 is observed in the initial 2 min (curve i)\(^9\). However, both the symmetry and amplitude of this signal gradually decreased in 10 min (curve ii), ascribing to the Mn(II) being oxidized when the H$_2$O$_2$ is in situ generated. Accordingly, a new signal around g = 4 corresponding to Mn(IV) species is observed, confirming the Mn(II) being oxidized to Mn(IV)\(^9\). Furthermore, the Mn(II) signals are barely observed after the light off for 10 min (curve iii) due to its consumption during the activation of H$_2$O$_2$ as well as the blocking of the regeneration of Mn(II) caused by the suspending of counterpart reduction reaction in cathode\(^10\).\(^11\). Significantly, the oxidation/reduction quasi-equilibrium reappears after reopening the light (curve iv), indicing the regeneration of Mn(II) from the Mn(IV) reduction under the photo-activated cathode\(^20\). As a result, it is unambiguously confirmed that the Mn species can be recycled as a “redox shuttle” under the solar-activated self-cycled system. In order to further evaluate the vital role of the self-cycled system, control experiments were conducted in the H-cell that separates the cathode and Mn species. As shown in Supplementary Fig. 3a, under continuous light illumination, the signal of Mn(IV) only appears in the H-cell, while a stable quasi-equilibrium of Mn(II)/Mn(IV) in the one-compartment opened reactor (Supplementary Fig. 3b).

To realize the on-site H$_2$O$_2$ production, the PEC water-oxidative H$_2$O$_2$ evolution and electrochemical oxygen-reductive H$_2$O$_2$ reaction are simultaneously employed. According to our previous reports, a SnO$_2$-x-coated BiVO$_4$ (SnO$_2$-x/BiVO$_4$) photocathode can kinetically favor the 2e$^-$ water oxidation reaction (2e$^-$ WOR) for H$_2$O$_2$ evolution accompanied by slight water-oxidative ·OH generation by 1e$^-$ WOR in a NaHCO$_3$ electrolyte because the SnO$_2$-x overlayer tunes the solid/liquid energetics\(^15\), and Mo-SACs/mrG, having the low thermodynamic barrier of 2e$^-$ oxygen reduction reaction (2e$^-$ ORR) for H$_2$O$_2$ evolution accompanied by slight water-oxidative ·OH generation by 1e$^-$ ORR in a NaHCO$_3$ electrolyte because the SnO$_2$-x overlayer tunes the solid/liquid energetics\(^15\), and Mo-SACs/mrG, having the low thermodynamic barrier of 2e$^-$ oxygen reduction reaction (2e$^-$ ORR), can present high activity and selectivity for electrochemical H$_2$O$_2$ generation in a NaHCO$_3$ electrolyte\(^15\). Here, to drive the 2e$^-$ ORR by solar light only, a SnO$_2$-x/BiVO$_4$/WO$_3$ photoanode is designed since the BiVO$_4$/WO$_3$ heterojunction is well-demonstrated to lower onset potential and increase photocurrent density\(^16\). Figure 2 shows a schematic diagram of the solar-driven H$_2$O$_2$ production device using a SnO$_2$-x/BiVO$_4$/WO$_3$ photoanode and a Mo-SACs/mrG cathode. By connecting the water-oxidative generation of H$_2$O$_2$ at the photoanode with the O$_2$-reductive

**Fig. 1 | Self-cycled photo-Fenton-like system with recycled Mn species.**

**a** Scheme of the Self-cycled photo-Fenton-like system with recycled Mn species. **b** EPR response of Mn species: (i) Mn(II) signal in the initial 2 min under AM 1.5 illumination. (ii) Mn(II)/Mn(IV) signal in the initial 10 min under AM 1.5 illumination. (iii) Mn(II)/Mn(IV) signals after 5 min since the light off. (iv) Mn(II)/Mn(IV) signals after 5 min since the light reopened.

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generation of H$_2$O$_2$ at the cathode, the photovoltage and photocurrent of the coupled photochemical reaction are constrained to be equal at the thermodynamic level. The redox potential of the BiVO$_4$/WO$_3$ photoanode electrode is 0.34 V vs. RHE and 2.43 V vs. RHE$^{28}$, which straddle the oxidation potential of the 2e$^-$ ORR (1.77 V vs. RHE) and the reduction potential of the 2e$^-$ WOR (1.76 V vs. RHE), which means that charge carriers excited by solar light can have enough energy to activate the overall reaction$^{21}$. The operating point for such a coupled photochemical reaction can be established at the intersection point of the independently measured J–V curves. As shown in Supplementary Fig. 4, the point of intersection corresponds to the operating current density, J$_{op}$. Considering the possible nonlinear correlation between the pH and redox potential, the SHyE should be calculated using H$_2$O$_2$ catalytic activity towards electrochemical 2e$^-$ ORR$^{33}$, a control sample denoted mrG was prepared via the same fabrication process used for Mo-SACs/mrG but without a metal source. Distinct RRDE tests of Mo-SACs/mrG are presented in Fig. 4a. The Tafel slope and onset potential (at a disk current density of 1 mA/cm$^2$) of Mo-SACs/mrG are 81 mV/dec and 0.61 V vs. RHE, respectively, while those of mrG are 81 mV/dec and 0.55 V vs. RHE, respectively (Fig. 4a and Supplementary Fig. 13). Furthermore, a much higher H$_2$O$_2$ selectivity was observed for in situ quantification of the H$_2$O$_2$ catalytic activity of the Mo-SACs/mrG catalysts. To exclude the impact of the carbonaceous substrate, which is proposed to serve as a potential catalyst toward electrochemical 2e$^-$ ORR$^{34}$, a control sample denoted mrG was prepared via the same fabrication process used for Mo-SACs/mrG but without a metal source. Distinct RRDE curves of Mo-SACs/mrG and mrG are presented in Fig. 4a. The Tafel slope and onset potential (at a disk current density of 1 mA/cm$^2$) of Mo-SACs/mrG are 81 mV/dec and 0.61 V vs. RHE, respectively, while those of mrG are 81 mV/dec and 0.55 V vs. RHE, respectively (Fig. 4a and Supplementary Fig. 13). Furthermore, a much higher H$_2$O$_2$ selectivity was observed for Mo-SACs/mrG compared to mrG from 0.35 to 0.65 V vs. RHE (Fig. 4b). Therefore, Mo-SACs/mrG was concluded to enable optimization of the intersection point of the J–V curve of the coupled photoanode and cathode with ideal H$_2$O$_2$ FE.

Prior to physically coupling the cathode and photoanode, the charge balance between the cathode and photoanode should be optimized since the activity of the cathode is limited by gas diffusion and electron transfer$^{35}$. Occasionally, a microporous gas diffusion layer (GDL) composed of PTFE and carbon-black powder is introduced between the active catalysts and carbon fiber to enhance the gas diffusion efficiency and boost the three-phase contact line (TPCL), on which the accessible active sites are functional. Nevertheless, a thick and insulated GDL will slow down electron transfer, resulting in serious ohmic loss and performance decay$^{36}$. Therefore, increasing the TPCL without hindering electron transfer is desirable. Herein, an interfacial
strategy is proposed to construct an oxygen local confinement structure on Mo-SACs/mrG nanosheets via PTFE nanoparticle decoration to increase the TPCL without inducing GDL (Fig. 4c and d). The PTFE@Mo-SACs/mrG-GDE cathode was characterized by SEM and HAADF-STEM, and the results are shown in Supplementary Fig. 14. The mrG nanosheets adhere tightly to the carbon fiber array, and PTFE nanoparticles with a size of ~150 nm are evenly distributed on the surface of mrG nanosheets, where single Mo atoms are the only metal species present (Supplementary Fig. 15). As illustrated in Supplementary Fig. 16, the quasi-nanoarray aerophilic area generated by the PTFE nanoparticle combined with Mo-SACs/mrG nanosheets is able to simultaneously contribute to compatible TPCL and significantly enhanced electron transfer compared to the conventional GDL electrode36,37. Further insights into the influence of PTFE on the electrocatalytic activity are obtained by altering the loading amount of the PTFE nanoparticles (Supplementary Fig. 17). Water contact angle tests reveal that the wettability of PTFE@Mo-SACs/mrG-GDE could be efficiently suppressed when the loading amount of PTFE increased (Supplementary Fig. 18), which is expected to accelerate gas diffusion. However, excessive PTFE loading deteriorates the conductivity of the electrode, as evidenced by EIS (Supplementary Fig. 19). Therefore, a delicate balance among the mass transfer of oxygen, the conductivity of the electrode and H2O2 formation efficiency is required for performance optimization. Ultimately, a 2:1 mass ratio of PTFE and Mo-SACs/mrG achieves the best performance, with a current density of 10 mA/cm2 at 0.51 V vs. RHE and a Tafel slope of 53.2 mV/dec (Supplementary Fig. 20). As a result, PTFE@Mo-SACs/mrG-GDE shows the highest current density in the voltage range from 0.65 to 0.1 V vs. RHE (Fig. 4c), with the smallest onset potential (0.51 V vs. RHE) and the largest H2O2 FE (82.1%) (Fig. 4e) compared to the Mo-SACs/mrG-GDL electrode (see "Methods for synthesis") and PTFE@mrG-GDE (see "Methods for synthesis"). Notably, the optimized PTFE@Mo-SACs/mrG-GDE cathode exhibits good electrochemical stability for the ORR, with 98.4% of the initial current maintained after 7 h (Supplementary Fig. 21).

After optimization of the H2O2 product selectivity, onset potential, and current density, the assembled SnO2-x/BiVO4/WO3||PTFE@Mo-SACs/mrG-GDE PEC cell for redox coupling of the 2e\(^{-}\)\(-\)WOR and 2e\(^{-}\)\(-\)ORR has a theoretical intersection point at 0.61 V vs. RHE at a current density of 1.64 mA/cm2 (Fig. 5a). The PEC performance was first investigated in a three-electrode system with SnO2-x/BiVO4/WO3 and PTFE@Mo-SACs/mrG-GDE as the photoanode and cathode, respectively. The linear sweep voltammetry (LSV) scan reveals a current density of 5.59 mA/cm2 at 1.76 V vs. RHE with a total H2O2 FE of 151% calculated from both the photoanode and cathode (Supplementary Fig. 22). Next, controlled potential tests were carried out to evaluate the H2O2 FE of the PEC device in a two-electrode system to evaluate the monolithic cell performance, and the results demonstrate a steady FE greater than 150% under a wide applied voltage range from 0 to 0.9 V vs. cell (Fig. 5b). Specifically, a bias-free photocurrent density of 1.56 mA/cm2 with an H2O2 FE of 152% was achieved (Fig. 5c), corresponding to an unassisted H2O2 production rate of 0.77 \(\mu\)mol/(min cm\(^2\)) and an SHyE of 1.46%. The difference from the theoretical value is attributed to the PEC limitation, such as the pH gradient, IR drop, and...
the polarization that occurs at the counter electrode in the two-electrode system ($\eta_r$ in Eq. (2))^34,38. As a result, an average solar-driven H$_2$O$_2$ production rate of 0.74 $\mu$mol/(min cm$^2$) is achieved, and the H$_2$O$_2$ concentration reached 0.85 mM within one hour in a 50 mL reactor (Fig. 5d). A summary of the PEC and solar-driven H$_2$O$_2$ production rate of our SnO$_2$/BiVO$_4$/WO$_3$/|PTFE@Mo-SACs/mrG-GDE PEC device (Fig. 5e and Supplementary Table 1), surpassing other state-of-the-art PEC systems^23,39. Potentiostatic $i$–$t$ tests were carried out under bias-free conditions and showed good stability of the PEC device, with 99% of the current retained after 20 h of H$_2$O$_2$ generation (Supplementary Fig. 23).

As a demonstration, a large SnO$_2$/BiVO$_4$/WO$_3$/|PTFE@Mo-SACs/mrG-GDE monolithic artificial leaf (7 cm$^2$) was engineered to enable a wastewater purification system with adequate H$_2$O$_2$ output (Fig. 6a). As shown in Fig. 6b, a significant improvement in current is observed when the areas of both the SnO$_2$/BiVO$_4$/WO$_3$ photoanode and PTFE@Mo-SACs/mrG-GDE cathode are increased to 7 cm$^2$, which yields a theoretical intersection point at 0.55 V vs. RHE and a current of 12.3 mA, indicating the good scalability of the PEC device, with 99% of the current retained after 20 h of H$_2$O$_2$ generation (Supplementary Fig. 24).

Fig. 4 | Catalysts and oxygen local confinement structure of the cathode for H$_2$O$_2$ production. a RRDE tests of Mo-SACs/mrG under O$_2$-purged 0.4 M NaHCO$_3$ electrolytes. b FE of H$_2$O$_2$ productions over Mo-SACs/mrG obtained by RRDE tests at various applied voltages. c LSV scan of the PTFE@Mo-SACs/mrG-GDE, PTFE@mG-GDE and Mo-SACs/mrG-GDL electrodes under an O$_2$-purged 0.4 M NaHCO$_3$ electrolyte. d Scheme of the structure of the PTFE@Mo-SACs/mrG-GDE electrode. e Potential at 10 mA/cm$^2$ and corresponding H$_2$O$_2$ FE of PTFE@Mo-SACs/mrG-GDE, PTFE@mG-GDE and Mo-SACs/mrG-GDL electrodes. The pentagram represents the H$_2$O$_2$ efficiency, and the blue rectangle represents the onset potential at 10 mA/cm$^2$. Nature Communications}
applied to explore the physicochemical properties of the photoanode after long-term testing. The SEM image shows the morphology of SnO$_2$-x/BiVO$_4$/WO$_3$ is well-maintained (Supplementary Fig. 31a) and a conformally and stable SnO$_2$-x overlayer on BiVO$_4$ is demonstrated (Supplementary Fig. 31b). Furthermore, EPR measurement evidence the maintenance of the oxygen vacancies of the SnO$_2$-x layer (Supplementary Fig. 31c). Moreover, XPS investigations on the composition of the surface and interfaces of SnO$_2$-x/BiVO$_4$/WO$_3$ were carried out. As shown in Supplementary Fig. 32a, the O1s peak shows no detectable changes in intensity and position, whereas a slight shift of the V 2p towards lower binding energy and reduced intensity can be observed after long-term testing. The phenomenon can be tracked to the photo-charging of BiVO$_4$ by which the V$^{5+}$ is somehow reduced to V$^{4+}$. Nevertheless, the Sn 3d peaks are determined to be stable during long-term testing (Supplementary Fig. 32b).

Further on, detailed and systematic studies have been performed to evaluate the ROSs generation/interconversion as well as the reaction mechanism in our self-cycled Fenton-like system. First, H-cell configuration was taken to specifically investigate the roles of 1O$_2$ and ·O$_2$ in the H$_2$O$_2$ production in both cathode and anode since both of them are common intermediates during the photocatalytic ORR for H$_2$O$_2$ production. For the cathode part, the scavenger experiments using p-benzoquinone (BQ, a sacrificial agent for ·O$_2$) and 2, 2, 6, 6-tetramethylpiperidine (TEMP, a sacrificial agent for 1O$_2$) over PTFE@Mo-SACs/mrG-GDE were performed. As shown in Supplementary Fig. 34a, b, the amount of the H$_2$O$_2$ is invariant with respect to the concentration of both BQ and TEMP, indicating that the quenching of either 1O$_2$ or ·O$_2$ has no effect on the H$_2$O$_2$ formation during the ORR in the cathode part. Similar experiment results were also observed in the anode part (Supplementary Fig. 34c, d) that neither the quenching of 1O$_2$ nor ·O$_2$ has impact on the generation of H$_2$O$_2$ during the WOR in
observed in the absence of Mn2+, even if H2O2 is effectively generated shown in Supplementary Fig. 36a, barely degradation effect is of ROSs between the system with and without Mn2+ species, which will at 40 min), indicating that the different interconversion mechanisms believed that the 1O2 and ·O2− might come from the ·OH in the system without Mn2+ species. On the other hand, the addition of Mn2+ species (28.1% at 40 min) compared to that without Mn2+ species (0.2% at 40 min), indicating that the different interconversion mechanisms of ROSs between the system with and without Mn2+ species, which will be further evaluated below.

To further investigate the role HCO3− in the generation of ROSs of the self-cycled photo-like system, KPi electrolyte with the same pH value (adjusted by KOH) is taken to replace NaHCO3 electrolyte. As shown in Supplementary Fig. 36a, barely degradation effect is observed in the absence of Mn2+, even if H2O2 is effectively generated in the reaction system (via 2e− ORR in cathode) (Supplementary Fig. 36b), which indicates KPi cannot activate H2O2 into ROSs as the HCO3− does (Fig. 6d and Supplementary Fig. S1). Furthermore, the degradation rate in KPi electrolyte slightly raised to 5.4% at 40 min when Mn2+ is added, which is still much lower than that in HCO3− electrolyte with Mn2+ (89.5% at 40 min). That means the effective activation of H2O2 is largely suppressed in the absence of HCO3−. EPR technology was employed to further investigate the mechanism. Methanol and DMPO were added as capture agents to exclude the interface of ·OH for detecting ·O2−. As shown in Supplementary Fig. 37a, no signals of ·O2− are detected in the system, indicating ·O2− not being generated. The signal intensities of ·O2− are unchanged after the addition of TEMP while being disappeared after the addition of TBA, indicating that the ·OH is essential for the generation of ·O2− while 1O2 is not (Supplementary Fig. 37b). Besides, no obvious signal is observed in the detection of ·O2− (Supplementary Fig. 37c). Moreover, the addition of TEMP and BQ has no impact on ·OH (Supplementary Fig. 37d). Therefore, the mechanism for the ROSs generation could be given:

\[
\text{HCO}_3^- + \text{H}_2\text{O}_2 \leftrightarrow \text{HCO}_4^- + \text{H}_2\text{O} \tag{4}
\]

\[
\text{HCO}_4^- + \text{H}_2\text{O}_2 \rightarrow \text{HCO}_3^- + \cdot \text{OH} + \text{HO}_2^- \tag{5}
\]

\[
\cdot \text{OH} + \text{HO}_2^- \rightarrow \cdot \text{O}_2^- + \text{H}_2\text{O} \tag{6}
\]

\[
\cdot \text{OH} + \cdot \text{O}_2^- \rightarrow ^1\text{O}_2 + \text{OH}^- \tag{7}
\]

On the other hand, the addition of Mn2+ in HCO3− electrolyte could largely increase the degradation rate by improving the generation of both ·O2− and ·OH (Fig. 6d and Supplementary Fig. S1). While the Mn2+ in KPi electrolyte shows a little effect of degradation (Supplementary Fig. 36a), indicating that the complex between Mn2+ and HCO3− plays the main role in the generation of the ROSs, which is also proved by the Fig. S1. EPR measurements were performed to further investigate the mechanism. Unlike in the HCO3− system, the addition of TBA has little impact on the generation of ·O2− and ·OH during the EPR measurements, indicating that ·OH is not essential for generating them in the Mn2+(HCO3−)n system (Supplementary Fig. 38a, b). However, the signal for ·O2− disappeared after the addition of BQ, indicating ·O2 come
from $\cdot O_2^-$ in the Mn$^{IV}$(HCO$_3^-$)$_n$ system (Supplementary Fig. 38a). Moreover, the addition of TEMP and BQ has no impact on $\cdot OH$ (Supplementary Fig. 38c). Above all, the ROSs generation in the Mn$^{II}$–HCO$_3^-$ system is given by:

$$\text{Mn}^{II} + \text{HCO}_3^- + \text{O}_2 \rightarrow \text{Mn}^{IV} + \text{CO}_2 + \text{H}_2\text{O}$$

In the self-cycled system, the transformation of Mn$^n$ species into Mn$^v$ species would be largely enhanced through Eq. (11) by the reduction of a cathode according to Fig. 1b and Supplementary Fig. S3.

$$\text{Mn}^{IV} + e^\text{(cathode)} \rightarrow \text{Mn}^{III}$$

**Discussion**

In summary, we report an unassisted solar-driven self-cycled photo-Fenton-like system through in situ production and utilization of $\text{H}_2\text{O}_2$ using an artificial leaf. First, we confirm that the Mn(II)/(IV) redox can be effectively recycled in the PEC system with the production of various ROSs, including $\cdot \text{OH}, \cdot \text{O}_2^-$ and $\cdot \text{O}_2$ driven by $\text{H}_2\text{O}_2$ activation and photoinduced cathode reduction under bicarbonate media. Next, in order to fulfill the adequate $\text{H}_2\text{O}_2$ supplement, comprehensive guidance toward enhancing PEC-to-$\text{H}_2\text{O}_2$ efficiency was emphasized with kinetic optimization of both the photoanode and cathode. Dramatically improved stability and current density due to the enhanced carrier transport were fulfilled in the photoanode, and an interfacial strategy was proposed to construct an oxygen local confinement structure to simultaneously benefit both the electron-transfer and mass-transfer processes at the cathode. As a result, the high recorded unassisted $\text{H}_2\text{O}_2$ production rate of 0.77 mmol/(min cm$^2$) and an SHyE of 1.46% were achieved by coupling the optimized photoanode and cathode. Especially, a 70-cm$^2$ artificial leaf with 30 days of stability was successfully realized as an effective self-cycled photo-Fenton-like system for wastewater treatment with the consumption of only oxygen, water, and sunlight. Notably, some improvements in this PEC-driven wastewater treatment system are needed for industrial-scale applications, including enhanced solar utilization efficiency, continuous oxygen supplement, and tuning electrolyte components. Therefore, additional discussion for addressing the above issues was carried out to identify the limitations, which are expected to be addressed to achieve further breakthroughs (see Supplementary discussion). Overall, the design of effective solar-fuel device presented here is expected to inspire further sustainable application, while the successful demonstration of a one-pot self-cycled wastewater treatment system highlights the promising potential of artificial photosynthesis technology in decentralized environmental governance applications.

**Methods**

**Synthesis of SnO$_2$x/BiVO$_4$/WO$_3$**

The WO$_3$ nanosheet array used as the template electrode was first synthesized by a modified hydrothermal method. Briefly, a precursor solution was prepared by slowly dropping 2 mL of 3.5 M HCl into 25 mL of 25 mM sodium tungstate dihydrate aqueous solution and allowing the reaction to occur for 1 min. Then, 25 mM ammonium oxalate was dissolved in the precursor solution and reacted for 15 min until the solution became completely transparent and colorless. Stirring was performed throughout the whole dissolution and reaction process. Then, a bare fluorine-doped tin oxide (FTO) substrates ($2 \times 2 \text{ cm}^2$) was placed against the Teflon wall before the solution was poured, and the hydrothermal reaction was carried out in a sealed 40 mL Teflon autoclave at 110 °C for 60 min. The obtained WO$_3$-H$_2$O$_2$ nanoray was washed with deionized (DI) water, dried, annealed at 500 °C in the air for 3 h, and cooled naturally to obtain the WO$_3$ nanoray. Next, the BiVO$_4$ precursor solution was synthesized by dissolving 100 mM bis-muth nitrate pentahydrate and 110 mM ammonium metavanadate in 20 mL of ethylene glycol. After that, a certain amount of BiVO$_4$ precursor solution was dropped onto the WO$_3$ photoanode (10 µL for 1 cm$^2$), followed by annealing at 500 °C in the air for 2 h and cooling naturally. Then, the obtained sample was placed into a 0.1 M NaOH solution to remove excessive vanadium oxide and obtain the BiVO$_4$/WO$_3$ photoanode. Finally, the SnO$_2$x layer was deposited according to our previous work to obtain the SnO$_2$x/BiVO$_4$/WO$_3$ photoanode.

**Synthesis of Mo-SACs/mrG and mrG**

Graphene oxide (GO) was synthesized by oxidation of natural graphite flakes according to a modified Hummers’ method. Mo-SACs/mrG was synthesized using a one-step process. In a specific procedure for synthesizing Mo-SACs/mrG, a pristine GO suspension was washed with DMSO several times to obtain a GO/DMSO solution with a GO concentration of 0.5 mg mL$^{-1}$. Then, 250 µL of 3 mg mL$^{-1}$ MoCl$_5$/DMSO was added to 30 mL of a 0.5 mg mL$^{-1}$ GO/DMSO solution. The homogeneous solution was transferred into a 50 mL Teflon-lined autoclave, which was sealed and maintained at 135 °C for 12 h in an oil bath. Finally, the resulting Mo-SACs/mrG was freeze-dried to obtain a powder after removing the DMSO solvent. The mrG was synthesized as same as Mo-SACs/mrG but without adding metal elements.

**Synthesis of PTFE@Mo-SACs/mrG-GDE**

The Mo-SACs/mrG ink was prepared by dissolving Mo-SACs/mrG powder in DI-water/ethanol/5 wt.% NaOH solution (volume ratio of 9:1:0.05) at a concentration of 1 mg/mL and stirring for 48 h. Then, the catalyst ink was obtained by adding a certain amount of poly tetrafluoroethylene (PTFE) aqueous solution (0.1 wt.% to the Mo-SACs/mrG ink and stirring for another 48 h to obtain Mo-SACs/mrG nanosheets with evenly distributed PTFE nanoparticles at the required mass ratio (PTFE@Mo-SACs/mrG). After that, the catalyst ink was dropped on the Teflon-treated hydrophobic carbon fiber (TCF) with a loading amount of 0.5 mg/cm$^2$, followed by natural drying to obtain PTFE@Mo-SACs/mrG-GDE.

**Synthesis of Mo-SACs/mrG-GDL electrode**

Mo-SACs/mrG-GDL electrode was prepared by dropping Mo-SACs/mrG ink on the gas diffusion layer coated carbon fiber with a loading amount of 0.5 mg/cm$^2$.

**Synthesis of PTFE@mG-GDE**

PTFE@mG ink was prepared the same as the PTFE@Mo-SACs/mrG-GDE except for changing the Mo-SACs/mrG into mrG.

**Synthesis of the artificial leaf**

For the wireless artificial leaf structure, an Ag paste-Cu sheet-Ag paste was used to connect the SnO$_2$x/BiVO$_4$/WO$_3$ photoanode to the PTFE@Mo-SACs/mrG-GDE cathode. Whole ohmic contacts were covered with epoxy for waterproofing.

**Material characterizations**

Scanning electron microscope (SEM) images were recorded on a field-emission scanning electron microscope (FESEM, JSM-7800F, Japan). X-ray diffraction (XRD) patterns were obtained with a D500/5000 diffractometer in Bragg-Brentano geometry under Cu Kα radiation. High resolution transmission electron microscope (HR-TEM) images were collected on a FEI Talos F200X JEOl electron microscope with energy-dispersive X-ray spectroscopy (EDS). High-angle annular dark field-scans transmission electron microscopy (HAADF-STEM) was performed on a JEOL JEM-ARM200F TEM/STEM (200 kV) with a spherical...
aberration corrector. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI-5000 VersaProbe II. The spectra were calibrated by the reference of the C1s peak at 284.8 eV. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were obtained via a UV–vis spectrometer (Shimadzu UV-3600 spectrophotometer) equipped with an integrating sphere. Electron paramagnetic resonance (EPR) measurements were carried out by a Bruker EMX plus spectrometer. The microwave power was 6.325 mW, microwave frequency was 9.826 GHz, and temperature was 298 K.

PEC measurements

There are two systems (a three-electrode system and a two-electrode system) for the photoelectrochemical (PEC) measurements to investigate the activity of photoanode/tandem device. Specifically, the three-electrode system was carried out using a photoanode as a working electrode, saturated Ag/AgCl as a reference electrode, and a carbonate electrode or designed cathode as a counter electrode, among which the designed cathode was taken as a counter electrode only in the tandem device. The two-electrode system was carried out to evaluate the tandem device using a photoanode as a working electrode and a cathode as a counter electrode. All potentials were converted to the reversible hydrogen electrode (RHE) reference scale by the equation $E_{(RHE)} = E_{(Ag/AgCl)} + 0.0591 \times \text{pH} + 0.197$. The illumination source was a 300 W Xe arc lamp with an AM 1.5G filter (100mW/cm2, FX 300, Beijing PerfectLight Co. Ltd). Electrochemical Impedance Spectroscopy (EIS) measurements were carried out with a AC perturbation of 10 mV applied over the frequency range of $10^{-2}$–$10^2$ Hz.

ORR measurements

Electrochemical oxygen reduction reaction (ORR) tests were performed in a CS2350H potentiostat (Corrtest, Wuhan) with a three-electrode cell at room temperature. A RRDE assembly (AFETR9GCPFT, Pine Instruments) consisting of a glassy carbon rotating disc electrode (Φ = 5.0 mm) and a Pt ring (Φ = 8.0 mm) was used, with a theoretical collection efficiency of 37%. A glassy carbon electrode loaded with catalyst was used as the working electrode. The working electrodes were prepared by dispersing the catalyst powder in ethanol and 5% Naflon 117 solution (20 μL of Naflon for 1 mL of ethanol) to achieve a catalyst concentration of 1 mg mL$^{-1}$. After sonication for 60 min, 7 μL of the catalyst ink was drop-dried onto a glassy carbon disc (area: 0.196 cm$^2$). The ORR activity and selectivity were investigated from polarization curves and RRDE measurements conducted in an oxygen-saturated electrolyte. The H$_2$O$_2$ selectivity was calculated using the following equation: $\eta(%) = \frac{200 \times \text{I}_{\text{ring}}}{\text{I}_{\text{disc}} + \text{I}_{\text{ring}}}$. The electron transfer number ($n$) at the disc electrode during the ORR was calculated using $n = 4 - \left(2 \times \text{I}_{\text{ring}} \right)$, where $\text{I}_{\text{ring}}$ is the ring current, $\text{I}_{\text{disc}}$ is the disc current and $\eta$ is the collection efficiency.

H$_2$O$_2$ production efficiency evaluation and organic dye degradation measurements

A H-type quartz reactor with two-compartment was used to evaluate both the anodic and cathodic H$_2$O$_2$ production efficiencies of the artificial leaf. The two-compartment reactor contained a 0.4 M NaHCO$_3$ solution in both the photoanode and cathode chambers separated by Naflon 117 membrane. The electrolyte solution in cathode chambers was first purged with pure O$_2$ for 30 min before testing, and the pure O$_2$ was continuously fed for stability testing. All current densities were normalized to the geometrical area of the photoanode. An integrated PEC system (PEC1000, Beijing Perfectlight Technology Co., Ltd.) with a solar simulator (AM 1.5G) was used.

The artificial leaf was placed in a single-compartment quartz reactor under AM 1.5 illumination with continuous O$_2$ purging to carry out the dye degradation tests, the electrolyte was 15 mL of 0.4 M NaHCO$_3$ solution containing 15 ppm NP and 0.04 ppm Mn(II) when the active area of the artificial leaf was 7 cm$^2$. Furthermore, the wastewater was changed to 200 mL of 0.4 M NaHCO$_3$ solution containing 5 ppm rhodamine B (Rh. B), 5 ppm methylene blue (MB), 5 ppm NP and 0.04 ppm Mn(II) when the active area of the artificial leaf was extended to 70 cm$^2$. Sample aliquots were taken at regular intervals and tested quickly. The concentration of 4-nitrophenol (NP), methylene blue (MB) and rhodamine B (Rh. B) were measured by an Ultraviolet-visible (UV-vis) spectrometer (PE Lambda 750 spectrophotometer).

**Quantification of H$_2$O$_2$**

H$_2$O$_2$ evolution was detected using the N,N-diethyl-1-4-phenylene-diamine (DPD) method. A stock solution of DPD was prepared by dissolving 0.1 g of DPD in 10 mL of a 0.05 M H$_2$SO$_4$ solution. A peroxidase (POD) solution was prepared by dissolving 10 mg of POD in 10 mL of deionized water and was kept in a refrigerator until use. A potassium phosphate buffer solution was prepared by mixing 49.85 mL of deionized water, 43.85 mL of 1 M monobasic potassium phosphate, and 6.3 mL of 1 M potassium phosphate. Sample aliquots (2 mL) were collected by a syringe during irradiation and mixed with 0.4 mL of potassium phosphate buffer solution, 3 mL of water, 0.05 mL of DPD, and 0.05 mL of POD and were shaken for 90 s. The obtained solutions were analyzed by Ultraviolet-visible (UV–vis) spectrometer (PE Lambda 750 spectrophotometer).

**Radical quenching tests**

The quenching tests for the identification of reactive oxygen species (ROSs) were carried out based on the EPR technology with different sacrificial agents: p-benzoquinone (BQ, a sacrificial agent for $\cdot$O$_2$), 2, 2, 6, 6-tetramethylperipiperide (TEMP, a sacrificial agent for $\cdot$O$_2$) and tert-butanol (TBA, a sacrificial agent for $\cdot$OH). The sacrificial agents were added before the reaction began and other steps were the same with experiments above.

**Data availability**

The data described in this paper are available from the authors upon reasonable request.

**References**

1. Parvulescu, V. I., Epron, F., Garcia, H. & Granger, P. Recent progress and prospects in catalytic water treatment. *Chem. Rev.* [https://doi.org/10.1021/acsrernrev.1c00527](https://doi.org/10.1021/acsrernrev.1c00527) (2021).
2. Shang, Y., Xu, X., Gao, B., Wang, S. & Duan, X. Single-atom catalysis in advanced oxidation processes for environmental remediation. *Chem. Soc. Rev.* [50], 5281–5322 (2021).
3. Xu, J. et al. Organic wastewater treatment by a single-atom catalyst and electrolytically produced H$_2$O$_2$. *Nat. Sustain.* [4], 233–241 (2021).
4. Li, L. et al. ROS-catalytic transition-metal-based enzymatic nanogents for tumor and bacterial eradication. *Adv. Funct. Mater.* [32], 2107530 (2021).
5. Thomas, N., Dionysiou, D. D. & Pillai, S. C. Heterogeneous Fenton catalysts: a review of recent advances. *J. Hazard. Mater.* [404], 124082 (2021).
6. Nagar, A. & Pradeep, T. Clean water through nanotechnology: needs, gaps, and fulfillment. *ACS Nanotechnol.* [14], 6420–6435 (2020).
7. Hodges, B. C., Cates, E. L. & Kim, J. H. Challenges and prospects of advanced oxidation water treatment processes using catalytic nanomaterials. *Nat. Nanotechnol.* [13], 642–650 (2018).
8. Yang, X. et al. The impact of peroxymonocarbonate (HCO$_4$) on the transformation of organic contaminants during hydrogen peroxide (H$_2$O$_2$) in situ chemical oxidation. *Environ. Sci. Technol.* [6], 781–786 (2019).
9. Richardson, D. E., Yao, H., Frank, K. M. & Bennett, D. A. Equilibria, kinetics, and mechanism in the bicarbonate activation of hydrogen peroxide: oxidation of sulfides by peroxymonocarbonate. *J. Am. Chem. Soc.* [122], 1729–1739 (2000).

https://doi.org/10.1038/s41467-022-32410-0
10. Sayama, K. Production of High-value-added chemicals on oxide semiconductor photoanodes under visible light for solar chemical conversion processes. ACS Energy Lett. 3, 1093–1101 (2018).
11. Xia, C. et al. Confined local oxygen gas promotes electrochemical water oxidation to hydrogen peroxide. Nat. Catal. 3, 125–134 (2020).
12. Liu, J., Zou, Y., Jin, B., Zhang, K. & Park, J. H. Hydrogen peroxide production from solar water oxidation. ACS Energy Lett. 4, 3094–3107 (2019).
13. Cheng, L. et al. Efficient H2O2 oxidation of organic dyes catalyzed by simple copper(II) ions in bicarbonate aqueous solution. Ind. Eng. Chem. Res. 53, 3478–3485 (2014).
14. Xu, A., Li, X., Ye, S., Yin, G. & Zeng, Q. Catalyzed oxidative degradation of methylene blue by in situ generated cobalt(II)-bicarbonate complexes with hydrogen peroxide. Appl. Catal. B 102, 37–43 (2011).
15. Dasgupta, J., Tsyryshkin, A. M., Kozlov, Y. N., Klimov, V. V. & Disnuxes, G. C. Carbonate complexation of Mn4+ in the aqueous phase: redox behavior and ligand binding modes by electrochemistry and EPR spectroscopy. J. Phys. Chem. B 110, 5099–5111 (2006).
16. Pan, H. et al. Recent advances in bicarbonate-activated hydrogen peroxide system for water treatment. Chem. Eng. J. 408, 127332 (2021).
17. Jeon, T. H. et al. Solar photoelectrochemical synthesis of electrolyte-free H2O2 aqueous solution without needing electrical bias and H2. Energ. Environ. Sci. 14, 3110 (2021).
18. Li, L., Hu, Z. & Yu, J. C. On-demand synthesis of H2O2 by water oxidation for sustainable resource production and organic pollutant degradation. Angew. Chem. Int. Ed. 59, 20538–20544 (2020).
19. Yim, M. B., Berlett, B. S., Chock, P. B. & Stadtmann, E. R. Manganese(II)-bicarbonate-mediated catalytic activity for hydrogen peroxide dismutation and amino acid oxidation: detection of free radical intermediates. Proc. Natl. Acad. Sci. USA 87, 394–398 (1990).
20. Rothbart, S., Ember, E. E. & van Eldik, R. Mechanistic studies on the oxidative degradation of orange II by peracetic acid catalyzed by simple manganese(II) salts. Tuning the lifetime of the catalyst. N. J. Chem. 36, 732–748 (2012).
21. Saadeh, S. M., Lah, M. S. & Pecoraro, V. L. Manganese complexes of α,α′-dihydroxy acids. Inorg. Chem. 30, 9–15 (2002).
22. John, R. P., Sreekantan, A., Kurup, M. R. & Fun, H. K. Chelating behavior of 2-hydroxyacetophenone N(4)-disubstituted thiosemicarbazones: facile formation of Mn(IV) complexes—X-ray structure, EPR and cyclic voltammetric studies. Polyhedron 24, 601–610 (2005).
23. Zhang, K. et al. Near-complete suppression of oxygen evolution for photoelectrochemical H2O2 oxidative H2O2 synthesis. J. Am. Chem. Soc. 142, 8641–8648 (2020).
24. Dong, C. et al. Precise synthesis of single atom (Mo, W, Nb) coordinated with oxygen functional groups of graphene oxide for stable and selective two-electrode oxygen reduction in neutral media. J. Mater. Chem. A https://doi.org/10.1039/D1TA01529A (2022).
25. Kim, J. H. & Lee, J. S. Elaborately modified BiO2O3 photoanodes for solar water splitting. Adv. Mater. 31, e1806938 (2019).
26. Sivula, K. & van, R. Semiconducting materials for photoelectrochemical energy conversion. Nat. Rev. Mater. 1, 15010 (2016).
27. Ifkovits, Z. P., Evans, J. M., Meier, M. C., Papadantonakis, K. M. & Lewis, N. S. Decoupled electrochemical water splitting systems: a review and perspective. Energ. Environ. Sci. 14, 4740–4759 (2021).
28. Xue, Y., Wang, Y., Pan, Z. & Sayama, K. Electrochemical and photoelectrochemical water oxidation for hydrogen peroxide production. Angew. Chem. Int. Ed. 60, 10469–10480 (2021).
29. Wang, Q., Pommérang, C., Linley, S. & Reisner, E. Strategies to improve light utilization in solar fuel synthesis. Nat. Energy 7, 13–24 (2021).
30. Barton, E. E., Rampulla, D. M. & Bocarsly, A. B. Selective solar-driven reduction of CO2 to methanol using a catalyzed p-GaP based photoelectrochemical cell. J. Am. Chem. Soc. 130, 6342–4 (2008).
31. Beranek, R. Selectivity of chemical conversions: do light-driven photoelectrocatalytic processes hold special promise? Angew. Chem. Int. Ed. 58, 16724–16729 (2019).
32. Trześniowski, B. J. et al. Near-complete suppression of surface losses and total internal quantum efficiency in BiVO4 photoanodes. Energy Environ. Sci. 10, 1517–1529 (2017).
33. Kim, H. W. et al. Efficient hydrogen peroxide generation using reduced graphene oxide-based oxygen reduction electrocatalysts. Nat. Catal. 1, 282–290 (2018).
34. Hodes, G. Photoelectrochemical cell measurements: getting the basics right. J. Phys. Chem. Lett. 3, 1208–1213 (2012).
35. Xu, W., Lu, Z., Sun, X., Jiang, L. & Duan, X. Superwetting electrodes for gas-involving electrocatalysis. Acc. Chem. Res. 51, 1590–1598 (2018).
36. Zhang, Q. et al. Highly efficient electrosynthesis of hydrogen peroxide on a superhydrophobic three-phase interface by natural air diffusion. Nat. Commun. 11, 1731 (2020).
37. Yu, J., Li, B. Q., Zhao, C. X., Liu, J. N. & Zhang, Q. Asymmetric air cathode design for enhanced interfacial electrocatalytic reactions in high-performance Zinc-air batteries. Adv. Mater. 32, e1908488 (2020).
38. Wang, Q. et al. Molecularly engineered photocatalyst sheet for scalable solar formate production from carbon dioxide and water. Nat. Energy 5, 703–710 (2020).
39. Jeon, T. H. et al. Solar photoelectrochemical synthesis of electrolyte-free H2O2 aqueous solution without needing electrical bias and H2. Energy Environ. Sci. 14, 3110–3119 (2021).
40. Pan, H. et al. Recent advances in bicarbonate-activated hydrogen peroxide system for water treatment. Chem. Eng. J. 408, 127332 (2021).
41. Jeon, T. H. et al. Solar photoelectrochemical synthesis of electrolyte-free H2O2 aqueous solution without needing electrical bias and H2. Energy Environ. Sci. 14, 3110–3119 (2021).
42. Fani, W. et al. Efficient oxidative hydrogen peroxide production. J. Am. Chem. Soc. 142, 8641–8648 (2020).
43. Dong, C. et al. Precise synthesis of single atom (Mo, W, Nb) coordinated with oxygen functional groups of graphene oxide for stable and selective two-electrode oxygen reduction in neutral media. J. Mater. Chem. A https://doi.org/10.1039/D1TA01529A (2022).
44. Kim, J. H. & Lee, J. S. Elaborately modified BiO2O3 photoanodes for solar water splitting. Adv. Mater. 31, e1806938 (2019).
45. Sivula, K. & van, R. Semiconducting materials for photoelectrochemical energy conversion. Nat. Rev. Mater. 1, 15010 (2016).
46. Ifkovits, Z. P., Evans, J. M., Meier, M. C., Papadantonakis, K. M. & Lewis, N. S. Decoupled electrochemical water splitting systems: a review and perspective. Energ. Environ. Sci. 14, 4740–4759 (2021).
47. Xue, Y., Wang, Y., Pan, Z. & Sayama, K. Electrochemical and photoelectrochemical water oxidation for hydrogen peroxide production. Angew. Chem. Int. Ed. 60, 10469–10480 (2021).
48. Wang, Q., Pommérang, C., Linley, S. & Reisner, E. Strategies to improve light utilization in solar fuel synthesis. Nat. Energy 7, 13–24 (2021).
49. Barton, E. E., Rampulla, D. M. & Bocarsly, A. B. Selective solar-driven reduction of CO2 to methanol using a catalyzed p-GaP based photoelectrochemical cell. J. Am. Chem. Soc. 130, 6342–4 (2008).
51. Hou, H., Zeng, X. & Zhang, X. Production of hydrogen peroxide by photocatalytic processes. Angew. Chem. Int. Ed. 59, 17356–17376 (2020).
52. Zhao, S. & Zhao, X. Insights into the role of singlet oxygen in the photocatalytic hydrogen peroxide production over polyoxometalates-derived metal oxides incorporated into graphitic carbon nitride framework. Appl. Catal. B 250, 408–418 (2019).
53. Ji, J. et al. Defects on CoS2−x: tuning redox reactions for sustainable degradation of organic pollutants. Angew. Chem. Int. Ed. 60, 2903–2908 (2021).
54. Guo, Z. et al. Single-atom Mn-N4 site-catalyzed peroxone reaction for the efficient production of hydroxyl radicals in an acidic solution. J. Am. Chem. Soc. 141, 12005–12010 (2019).
55. Che, H. et al. Iodide-induced fragmentation of polymerized hydrophilic carbon nitride for high-performance quasi-homogeneous photocatalytic H2O2 production. Angew. Chem. Int. Ed. 60, 25546–25550 (2021).

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Author contributions
K.Z. and J.H.P. conceived and designed the experiments. Y.H.A. and J.Y.S. conducted the dye degradation measurement and analysis, C.R.D. and L.Y.W. carried out materials synthesis and electrochemical characterization. Y.L.Y. and X.M.H. participated in part of the synthesis. Y.C. and G.J. carried out materials characterization. K.Z., C.R.D., Y.H.A., and J.H.P. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Yanhui Ao, Jong Hyeok Park or Kan Zhang.

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