

Nicotiana tabacum growth promotion by water oxidation modulated artificial photosynthesis with Ru-Oxo clusters decorated g-C₃N₄ nanosheets

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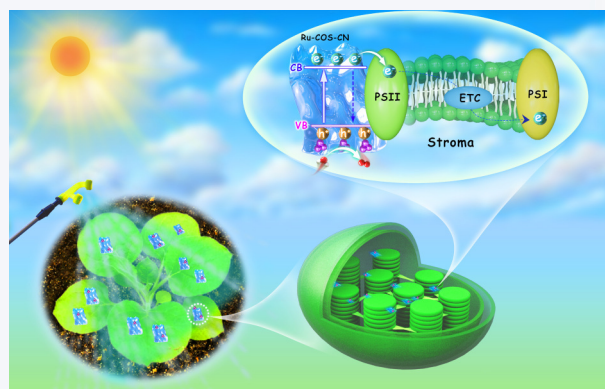
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ABSTRACT: Artificial photosynthesis is highly desired to enhance natural photosynthesis, but it still faces enormous challenges stemming from the sluggish water oxidation process. Herein, biocompatible g-C₃N₄ nanosheets decorated by ultra-small Ru-Oxo clusters (Ru-COS-CN) were synthesized using tailored chitosan oligomers, and were applied to foliar spray for promoting photosynthesis of tobacco. The tobacco growth exhibited a positive correlation with the water oxidation performance of the photocatalysts, leading to the growth promotion of 36.1%, 36.8%, 27.4%, and 15.9% per 10 days for average fresh weight, dry weight, plant length, and leaf area with Ru-COS-CN treatment, respectively. The promotion is attributed to the produced long-lifetime photoelectrons from the utilized light range extension and the accelerated photocatalytic water oxidation by means of *in situ* μ s-transient absorption spectra, and to the effective electron transfer into the chloroplasts with an enhanced electron transfer rate in the electron transport chain based on the results of Hill reaction.



KEYWORDS: g-C₃N₄ nanosheet, Ru-Oxo cluster modification, water oxidation, charge transfer, tobacco growth

1 Introduction

The shortage of fossil energy and the increase in environmental pollution raise an ever-growing desire for the efficient utilization of solar energy. Natural photosynthesis stands out as one of the most successful processes to convert solar energy to chemical energy, which is essential process for the growth and development of plant or organism system. This complex biochemical process involves

both light and dark reactions, enabling plants to absorb light energy, carbon dioxide, and water to produce organic matter, which in turn provide energy for plant growth and development [1]. However, only 400–700 nm wavelength range can be defined as photosynthetically active radiation to perform this biochemical process, and the conversion efficiency of solar energy to chemical energy is extremely limited. Consistent efforts have been made to promote plant growth and increase crop yields, generally through the application of fertilizers and other methods. Nevertheless, these approaches often result in increased costs. It should be pointed out that the absorbed light of chloroplasts is limited to visible light spectrum [2]. In contrast, the solar spectrum, spanning from ultraviolet to visible light, offers considerable potential for further utilization. To address this, various fluorescent conversion materials have been developed to extend the range of usable solar energy. Li et al. reported the preparation of far-red emissive carbon dots

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(FR-CDs), which can convert absorbed ultraviolet A (UV-A) into far-red light, thereby enhancing the utilization of sunlight by Roman lettuce [3]. Wang et al. developed a bio-optical hybrid photosynthesis system by coating chloroplasts with conjugated polymer nanoparticles (chloroplast/CPNs). CPNs can strongly absorb ultraviolet light and emit visible light that chloroplasts could absorb, further enhancing solar energy conversion [4]. Whereas, the light conversion efficiency is still unsatisfactory owing to the challenge on the compatibility with the absorption wavelength of plant photosynthesis.

In recent years, photocatalysis, also known as artificial photosynthesis, has attracted widespread attention. Semiconductors, as the core of photocatalysis, utilize light energy to generate photogenerated electron-hole pairs, initiating a series of redox reactions, such as H_2O splitting [5], CO_2 reduction [6,7], and N_2 fixation [8]. Therefore, it is expected to further promote natural photosynthesis by broadening the spectral utilization range through photocatalysis. In natural photosynthesis, the water oxidation reaction, which occurs in photosystem II (PS II), is a critical step. During this process, plants use sunlight to split water into oxygen, protons, and electrons at the oxygen evolving catalytic site [9, 10]. These protons and electrons are subsequently transferred through the electron transport chain, generating energy–adenosine triphosphate (ATP) and reducing force–reduced nicotinamide adenine dinucleotide phosphate (NADPH) that drive carbon fixation in the dark reaction [11–13]. As such, the activity of PS II plays a significant role in determining crop yields. However, the sluggish water oxidation reaction within PS II, which critically affects the electron transfer rate (ETR) in the electron transport chain (ETC), ultimately reduces the overall photosynthesis activity. This process naturally draws a parallel with water oxidation in artificial photosynthesis. Actually, the photocatalytic oxygen evolution reaction in artificial photosynthesis is similarly a slow process, involving multi-electron and multi-proton transfers with a reaction time of approximately one second [14]. Therefore, the key to promoting natural photosynthesis through artificial photosynthesis is to extend the range of solar light utilization as well as to accelerate the water oxidation process by well-designed photocatalyst. In particular, it is more meaningful for photocatalysts to drive water oxidation reactions by absorbing UV light, which maximizes solar energy utilization and enhances photosynthesis without overlapping with the light absorption range of plants. Furthermore, the biocompatibility and interfacial relationships also need to be considered.

Among the various photocatalysts explored to date, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$ or CN) has been intensively investigated for artificial photosynthesis due to its good stability, abundant availability, and high tunability [15–18]. As an organic polymer semiconductor, CN exhibits excellent biocompatibility, making it a potential nanomaterial for enhancing natural photosynthesis. More importantly, with its strong absorption of UV light, CN supplements the range of sunlight that plants can utilize. However, bulk CN is often hindered by high recombination rate of photoinduced carriers, severely limiting its photocatalytic activity [19, 20]. In contrast, ultrathin CN nanosheets reduce the recombination of photogenerated charge carriers due to their shortened diffusion distance [21]. Moreover, the intrinsic lack of catalytic sites makes it challenging for CN to achieve the water oxidation reaction, owing to high energy barriers, slow kinetics, as well as the uphill reaction thermodynamics [22, 23]. Until now, it

remains a bottleneck for solar fuels synthesis under sacrificial agent-free conditions. Typically, the introduction of a co-catalyst is an effective strategy to accelerate water oxidation, as it can capture photogenerated holes, promoting charge separation and reducing the overpotential for the water oxidation reaction. Based on the volcano plot of the binding energy of oxygen intermediates, iridium oxide (IrO_2) and ruthenium oxide (RuO_2) are among the most active oxygen evolution reaction (OER) cocatalysts reported to date [24, 25]. To strike a balance between cost and activity, Ru emerges as an optimal selection within the platinum group. Intriguingly, transitioning from RuO_2 nanoparticles to sub-nano metal clusters can increase the number of exposed atoms, further improving catalytic performance, but it remains challenging. To obtain ultrasmall Ru-based sub-nano clusters on CN, it is essential to identify a linker with functional groups that can effectively coordinate and stabilize the ultrasmall metal species. Additionally, the strong interfacial bonding between the photocatalyst and the plant leaves will prolong the residence time of the photocatalyst on the leaves, which is crucial for its catalytic efficiency. Therefore, a linker that can anchor metal ions while simultaneously ensuring robust interfacial contact with plant leaves is of great importance.

Chitosan (CS), a natural polysaccharide composed of glucosamine and N-acetyl glucosamine units linked by glycosidic bonds, has garnered significant interest in various fields, including chemistry, biotechnology, and medicine, due to its biocompatibility, metal ion-binding capacity, and biodegradability [26–29]. The abundance of $-\text{NH}_2$ and $-\text{OH}$ groups on the CS chain makes it an excellent chelating agent for efficient anchoring with metal ions, which holds great potential as a versatile platform for supporting active species. Furthermore, the numerous hydrophilic groups confer adhesive properties, facilitating strong interactions between the photocatalyst and plant leaves [30]. Consequently, CS is an ideal candidate as both a coordination agent and binder, achieving the dual functions of anchoring ultra-small sub-nano oxygen-bearing clusters and establishing a tightly connected interface with plant leaves. In our previous work [31], tailored chitosan oligomers were employed to anchor transition metal species on ultrathin CN nanosheets through $-\text{OH}$ and $-\text{NH}_2$. Notably, the introduction of Mn-Oxo species has been shown to effectively capture photogenerated holes and facilitate water activation. Therefore, it is anticipated that ultrasmall sub-nano Ru-Oxo clusters can similarly be anchored on CN, potentially enhancing performance of water oxidation reactions. Based on the above considerations, numerous long-lived photogenerated electrons will be generated through the extension of sunlight utilization and the accelerated water oxidation process. These electrons will subsequently be transferred to the chloroplasts with an enhanced ETR in the ETC, and thus promoting plant growth.

Herein, highly uniform Ru-Oxo cluster-anchored CN nanosheets (Ru-COS-CN) were successfully synthesized and, for the first time, sprayed on tobacco (*Nicotiana tabacum* L.) leaves to promote their growth. Tobacco growth was largely promoted, with the average fresh weight, dry weight, plant length, and leaf area increase by 36.1%, 36.8%, 27.4%, and 15.9% per 10 days, respectively, following Ru-COS-CN treatment. The extended light absorption range and the boosted photocatalytic water oxidation process of the photocatalysts prolong the lifetime of photogenerated electrons, enable effective electron transfer from Ru-COS-CN to the tobacco chloroplasts with an enhanced ETR in the ETC, and ultimately promote tobacco growth. This work provides a

promising strategy to enhance the photosynthetic efficiency and improve crop yields by engineering photocatalysts with improved sunlight utilization and robust water oxidation activities.

2 Experimental

2.1 Synthesis of ultrathin carbon nitride nanosheets

Ultrathin carbon nitride ($g\text{-C}_3\text{N}_4$) nanosheets were synthesized following a previously reported method [32]. In a typical procedure, 35.0 g of urea was placed in a ceramic crucible and calcined in a muffle furnace at 550 °C for 3 h (ramp rate: 0.5 °C·min⁻¹). The resulting pale-yellow powder was then finely ground and subjected to a second calcination in a semi-closed porcelain boat at 500 °C for 2 h (ramp rate: 5 °C·min⁻¹). After natural cooling to room temperature, 1.0 g of the obtained material was placed in a round bottom flask containing 100 mL of nitric acid solution (5 M) and refluxed at 120 °C for 2 h. After that, the refluxed white products were centrifuged and washed with deionized water until the pH of the supernatant approached neutral. The product was then dried in an oven at 80 °C, yielding ultrathin $g\text{-C}_3\text{N}_4$ nanosheets, referred to as CN.

2.2 Synthesis of COS-CN

A total of 0.2 g of as-prepared CN was dispersed in 20 mL of deionized H₂O. Subsequently, tailored chitosan oligomers (COS) (5.0 wt.% relative to CN) were added to the above solution, and the mixture was stirred magnetically for 5 h [31]. The resulting suspension was then transferred to a stainless-steel vessel and maintained at 120 °C for 2 h. After natural cooling to room temperature, the product was collected by centrifugation, washed with absolute ethanol, and then dried at 60 °C overnight. The samples were denoted as COS-CN.

2.3 Synthesis of Ru-COS-CN and Mn-COS-CN

A total of 0.2 g of COS-CN was dispersed in 20 mL of deionized H₂O under constantly stirring. A certain amount of RuCl₃ solution was then added to the suspension and stirred for 5 h. Subsequently, the resulting aqueous suspension was transferred to a stainless-steel vessel and kept at 120 °C for 2 h. After natural cooling to room temperature, the resulting product was centrifuged, washed with deionized water and absolute ethanol, and then dried in an oven at 60 °C. The samples were denoted as $x\text{Ru-COS-CN}$, where x represents the mass percentage of Ru relative CN. In this work, the optimized 2Ru-COS-CN photocatalyst was abbreviated as Ru-COS-CN and was characterized and analyzed unless otherwise specified. The synthesis of Mn-COS-CN followed the same procedure, with Mn(NO₃)₂ as the precursor. The molar ratio of Mn to CN was

consistent with that of Ru, and the optimal mass ratio of Mn to CN was 1.0%, as determined in our previous study [31].

2.4 Photocatalytic activities for oxygen evolution reaction

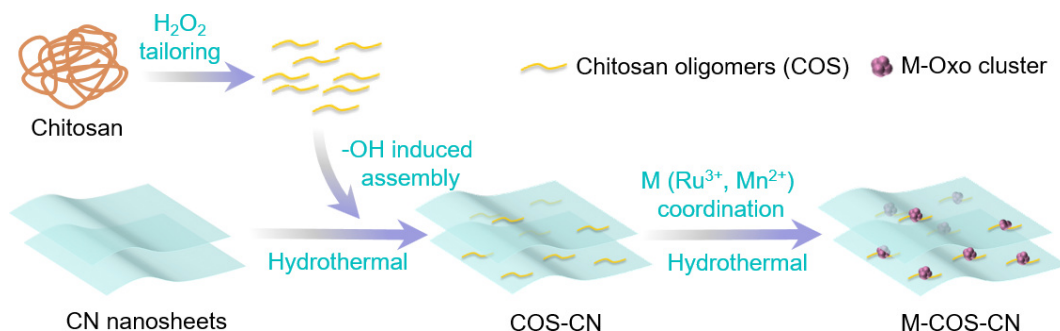
The photocatalytic oxygen evolution experiment was performed on an external irradiation Pyrex photoreactor equipped with a top window and connected to a closed gas circulation system (Perfectlight, Labsolar-6A circulation system, Beijing). Typically, 50 mg of photocatalyst and 200 mg of La₂O₃ were dispersed in 100 mL of 0.1 M AgNO₃ aqueous solution, with constant stirring to prevent the photocatalyst from settling. Prior to irradiation, the photocatalytic reactor was evacuated to remove any air and dissolved gas. A 300 W Xenon lamp was used as the light source to irradiate the solution, and the evolved oxygen was analyzed using an on-line gas chromatograph (Techcomp GC-2002) equipped with a thermal conductivity detector (TCD), a 6 Å molecular sieve column, and argon as the carrier gas. The temperature of the photocatalytic reaction system was maintained at 5 °C throughout the photocatalytic reaction process using a cooling water circulation system.

2.5 Cultivation of tobacco and foliar application of photocatalysts

Tobacco was selected and cultivated as a model plant to evaluate the effect of photocatalysts on plant growth. Prior to planting, all soil and flowerpots were sterilized. Tobacco seeds were disinfected in sodium hypochlorite solution (5.0 wt.%) for 20 min and subsequently rinsed three times with deionized water. After soaking for 12 h, the swollen tobacco seeds were sown in sterilized soil within flowerpots, which were kept in a controlled environment with 60% humidity, 23–24 °C, and no light for 24 h. After that, the flowerpots were placed under plant growth light source (Philips, LED PAR38) for tobacco seeds to germinate and grow. After 5–6 days, the tobacco seedlings began to sprout. When it had grown to 3–4 leaves, phenotypically similar tobacco seedlings were selected for conducting foliar spraying of photocatalysts. Every 5 days, 2 mL of the photocatalyst suspension was sprayed onto the tobacco leaves at a given concentration. For each concentration (photocatalysts), two experimental groups of tobacco were set up and allowed to grow for 10 and 20 days, respectively. These tobaccos were then harvested for further measurements, with deionized water serving as the control.

3 Results and discussion

The synthetic paradigm of M-COS-CN nanosheets is illustrated in Scheme 1. Firstly, CN nanosheets were synthesized through a two-step calcination process using urea as the raw material, followed by



Scheme 1 Schematic illustration of the synthetic process of M-COS-CN photocatalysts.

exfoliation through nitric acid post-treatment. Next, COS molecules, tailored from chitosan through H_2O_2 treatment, were functionalized onto CN nanosheets through a facile hydroxyl-induced assembly procedure, forming COS-CN. Finally, metal oxygen-bearing clusters (M-Oxo) were further modified onto COS-CN by coordinating metal M (Ru^{3+} , Mn^{2+}) with the $-\text{OH}$ and $-\text{NH}_2$ groups of COS molecules, yielding the final M-COS-CN photocatalysts.

3.1 Effect of CN, Mn-COS-CN, and Ru-COS-CN nanosheets on tobacco growth

Tobacco was cultivated as model plant and the growth behavior of

tobacco fostered with different concentrations of Ru-COS-CN nanosheet suspensions (0 (CK), 50 , 100 , $200 \text{ mg}\cdot\text{L}^{-1}$) was evaluated on days 10 and 20. As shown in Figs. 1(a) and 1(b), both fresh and dry weights increased with concentrations from 50 to $100 \text{ mg}\cdot\text{L}^{-1}$ of Ru-COS-CN treatment, but decreased at concentration above $100 \text{ mg}\cdot\text{L}^{-1}$. The inhibition of tobacco growth under high Ru-COS-CN concentrations may be due to its effects on stomatal conductance and a light-shielding effect, which consequently reduces photosynthesis in tobacco. This suggests a growth promoting potential within a controlled concentration range of Ru-COS-CN. Figure S1 in the Electronic Supplementary Material (ESM) displays the phenotype of tobacco treated with CN,

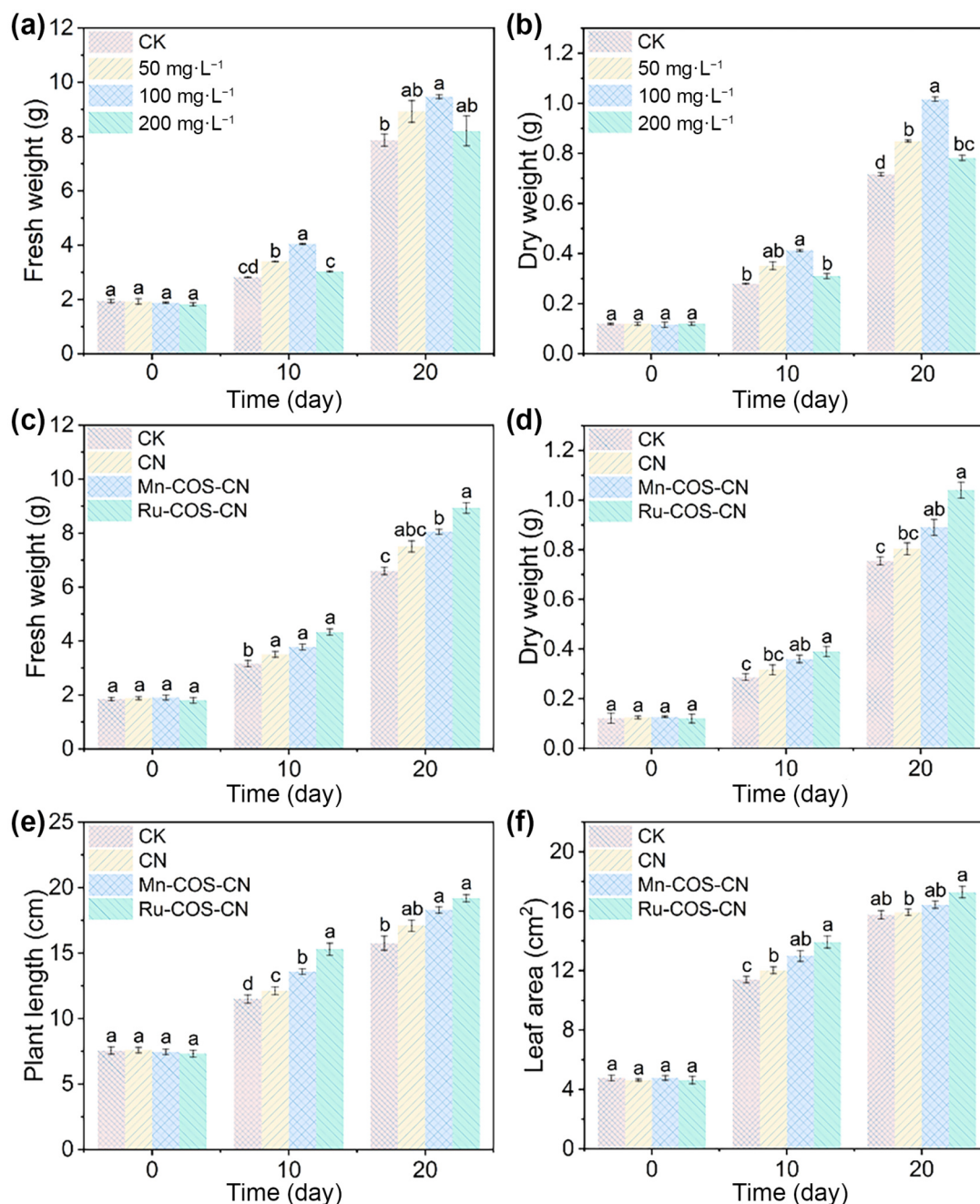


Figure 1 Impact of photocatalysts on tobacco growth. (a) Fresh weight and (b) dry weight of tobacco treated with different concentrations of Ru-COS-CN. (c) Fresh weight, (d) dry weight, (e) plant length, and (f) leaf area of tobacco treated with $100 \text{ mg}\cdot\text{L}^{-1}$ of CN, Mn-COS-CN, and Ru-COS-CN. The values are presented as mean $\pm$ SD. Significant differences among treatments are indicated with different letters.

Mn-COS-CN, and Ru-COS-CN nanosheets at the optimal concentration of $100 \text{ mg}\cdot\text{L}^{-1}$, where Ru-COS-CN treatment exhibited the most substantial growth enhancement. Quantitative measurements of the fresh weight, dry weight, plant length, and leaf area after foliar spraying of each photocatalysts (CN, Mn-COS-CN, Ru-COS-CN nanosheets) are shown in Figs. 1(c)–1(f), revealing significantly growth promotion compared to CK. The Ru-COS-CN photocatalyst exhibits the most prominent enhancement with fresh weight by 36.1%, dry weight by 36.8%, plant length by 27.4%, and leaf area by 15.9% per 10-day interval.

3.2 Morphology and structural characterizations of photocatalysts

To gain a deeper insight into the mechanisms by which M-COS-CN promotes plant growth, the structure of M-COS-CN was thoroughly analyzed. X-ray diffraction (XRD) patterns of CN, Mn-COS-CN, and Ru-COS-CN (Fig. S2(a) in the ESM) show characteristic peaks at 13.1° and 27.3° , corresponding to the in-planar repeated tri-s-triazine units (100) and the interlayer stacking (002) of CN [33], with no changes observed following M-Oxo modification. UV-vis absorption spectra show that the modification of Ru-Oxo and Mn-Oxo does not affect the light absorption of CN (Fig. S2(b) in the ESM). Interestingly, compared with the absorption of chloroplasts, Ru-COS-CN supplements the absorption of the UV light in sunlight (Fig. S3 in the ESM). X-ray photoelectron spectroscopy (XPS) further reveals the chemical states of Mn-Oxo and Ru-Oxo clusters. As shown in Fig. S2(c) in the ESM, the C 1s spectrum shows peaks at 282.1 and 285.8 eV, corresponding to Ru $3d_{5/2}$ and Ru $3d_{3/2}$, indicative of Ru^{3+} oxidation states [34]. The Mn 2p peaks at 641.6 and 652.0 eV are associated with oxidized Mn^{2+} species in Mn-COS-CN (Fig. S2(d) in the ESM) [35]. Transmission electron microscopy (TEM) image reveals a two-dimensional (2D) sheet-like morphology for Ru-COS-CN (Fig. 2(a)), while high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Fig. 2(b)) and Fig. S4 in the ESM) confirms the presence of uniform, ultra-small Ru-Oxo clusters with an average diameter of $\sim 1.7 \text{ nm}$. The absence of aggregates or larger particles highlights that COS pre-functionalization provides effective sites for Ru^{3+} coordination,

facilitating controlled anchoring of small clusters on CN. Energy dispersive X-ray (EDX) element mapping validates the uniform distribution of key elements (C, N, O, and Ru) across the CN surface (Fig. 2(e)). The atomic force microscopy (AFM) image confirms that the average thickness of Ru-COS-CN is determined to be $\sim 3.3 \text{ nm}$ (Figs. 2(c) and 2(d)), favorable for efficient photogenerated charge carrier transfer. The structure of Ru-COS-CN nanosheets after ultrasonic dispersion is shown in Fig. S5 in the ESM.

As revealed by HAADF-STEM, COS molecules effectively anchor ultra-small Ru-Oxo clusters. Notably, the abundant hydrophilic groups in COS could contribute to enhanced interaction with the tobacco leaf. As depicted in Fig. S6 in the ESM, the average contact angle of CN was 48° , while COS-CN exhibited a reduced contact angle of 45° , indicating a more compact interaction between the photocatalyst and the leaf surfaces. Figure S7 in the ESM displays the photographs of tobacco leaves sprayed with Ru-COS-CN nanosheets before and after rinsing with water. It can be clearly seen that the Ru-COS-CN nanosheets are evenly distributed on the tobacco leaves, and no obvious changes can be observed after rinsing, further demonstrating this strong interaction.

3.3 Water oxidation performance and charge transfer of photocatalysts

The water oxidation performance of photocatalysts was evaluated under 300 W Xenon lamp irradiation in a 100 mL aqueous solution containing AgNO_3 as the sacrificial electron acceptor, with La_2O_3 powder added to keep neutral conditions. As shown in Fig. S8(a) in the ESM, COS-CN exhibits slightly higher oxygen evolution rates than CN. Accordingly, COS-CN shows a reduced photoluminescence (PL) intensity compared to CN, indicating an enhancement in charge separation facilitated by the COS functionalization (Fig. S8(b) in the ESM). This enhanced charge separation accounts for the observed improvement in the oxygen evolution rate. Based on the premodification of COS, a series of $\alpha\text{Ru-COS-CN}$ nanosheets were successfully synthesized with different Ru-Oxo loadings. The introduction of Ru-Oxo significantly enhances the charge separation and photocatalytic performance of CN, with 2.0Ru-COS-CN achieving the highest

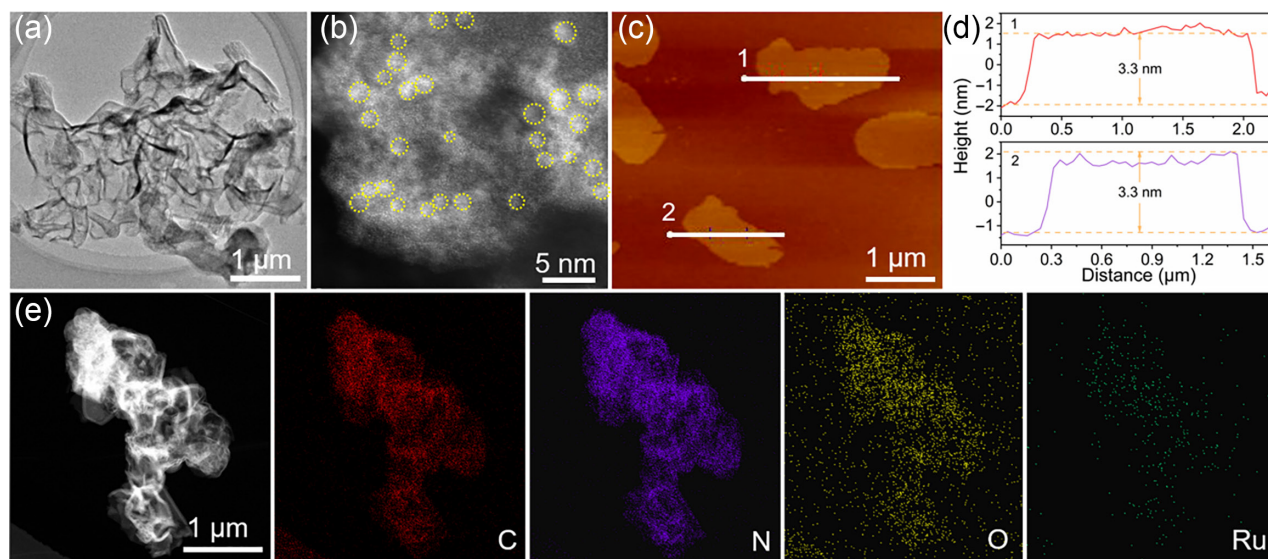


Figure 2 Morphology and structural characterization of Ru-COS-CN. (a) TEM image, (b) HAADF-STEM image, (c) AFM image, and (d) corresponding height profiles of Ru-COS-CN nanosheets. (e) STEM image and the corresponding EDX mapping images of Ru-COS-CN.

oxygen generation rate and superior charge separation (Fig. S9 in the ESM). Based on our previous work, 1.0Mn-COS-CN nanosheets with an optimal Mn-Oxo loading amount were fabricated for comparison [31]. As shown in Fig. 3(a), the modification of M-Oxo on CN demonstrates an improvement in the oxygen evolution rate, while Ru-COS-CN exhibits a more remarkable enhancement, with a 15-fold increase in oxygen evolution rate compared to CN. Figure S10 in the ESM illustrates that introducing both Mn-Oxo and Ru-Oxo clusters promotes charge separation, with Ru-COS-CN achieving the highest degree of charge separation relative to CN and Mn-COS-CN. Time-resolved photoluminescence (TR-PL) results in Fig. 3(b) and Table S1 in the ESM further support these findings, revealing an average PL lifetime of 7.49 ns for Ru-COS-CN, compared to 8.80 ns for Mn-COS-CN and 9.28 ns for CN. These observations indicate that Mn-Oxo and Ru-Oxo clusters facilitate the charge transfer and separation, supporting improved photocatalytic performance [36].

The specific role of Ru-Oxo clusters in promoting charge separation was evaluated by atmosphere-controlled surface photovoltage spectroscopy (AC-SPS). Figure 3(c) shows an obvious SPS response for Ru-COS-CN in N_2 , while the response decreases in the presence of O_2 , which is known to capture photoelectrons. This reduction suggests that Ru-Oxo clusters facilitate charge separation by capturing photogenerated holes, counteracting the electron capture effect of O_2 . Furthermore, electrochemical oxidation measurements reveal the catalytic activity of Mn-Oxo and Ru-Oxo clusters. The onset potential sequence Ru-COS-CN < Mn-COS-CN < CN (Fig. 3(d)) indicates that Ru-COS-CN most effectively lowers the activation barriers for catalytic water

oxidation. Collectively, these findings reveal a positive correlation between the performance of photocatalytic water oxidation and the enhancement of tobacco growth. In addition, no obvious change in the surface temperature of tobacco leaves was observed before and after Ru-COS-CN treatment with increasing irradiation time, indicative of its negligible thermal effect (Fig. S11 in the ESM).

To further validate these findings, the traditional water oxidation cocatalyst RuO_2 were loaded onto CN and employed to investigate their impact on tobacco growth. As shown in Fig. S12(a) in the ESM, RuO_2 -CN retains the characteristic 2D sheet-like morphology, and the lattice fringes with a spacing of 0.18 nm were observed on the high-resolution TEM image corresponding to the (211) lattice plane of RuO_2 (Fig. S12(b) in the ESM) [37], confirming the successful modification of RuO_2 on CN. However, the nanosized RuO_2 particles (~ 20 nm) are much larger than the sub-nano Ru-Oxo clusters, which demonstrates the effective role of COS in anchoring metal species and inhibiting their aggregation. Additionally, XRD and UV-vis absorption spectra demonstrate that RuO_2 modification does not alter the structure or optical absorption properties of CN (Figs. S12(c) and S12(d) in the ESM).

Compared to Ru-COS-CN, RuO_2 -CN shows a lower fluorescence spectroscopy (FS) intensity, as shown in Fig. S12(e) in the ESM, indicating a reduced charge separation capability. Consequently, RuO_2 -CN displays lower oxygen evolution rates than Ru-COS-CN, suggesting that the ultra-small and uniformly distributed Ru-Oxo clusters anchored by COS more effectively enhance photogenerated charge separation and improve OER performance (Fig. S12(f) in the ESM). Notably, the foliar spraying of RuO_2 -CN also promotes tobacco growth. As seen from Figs.

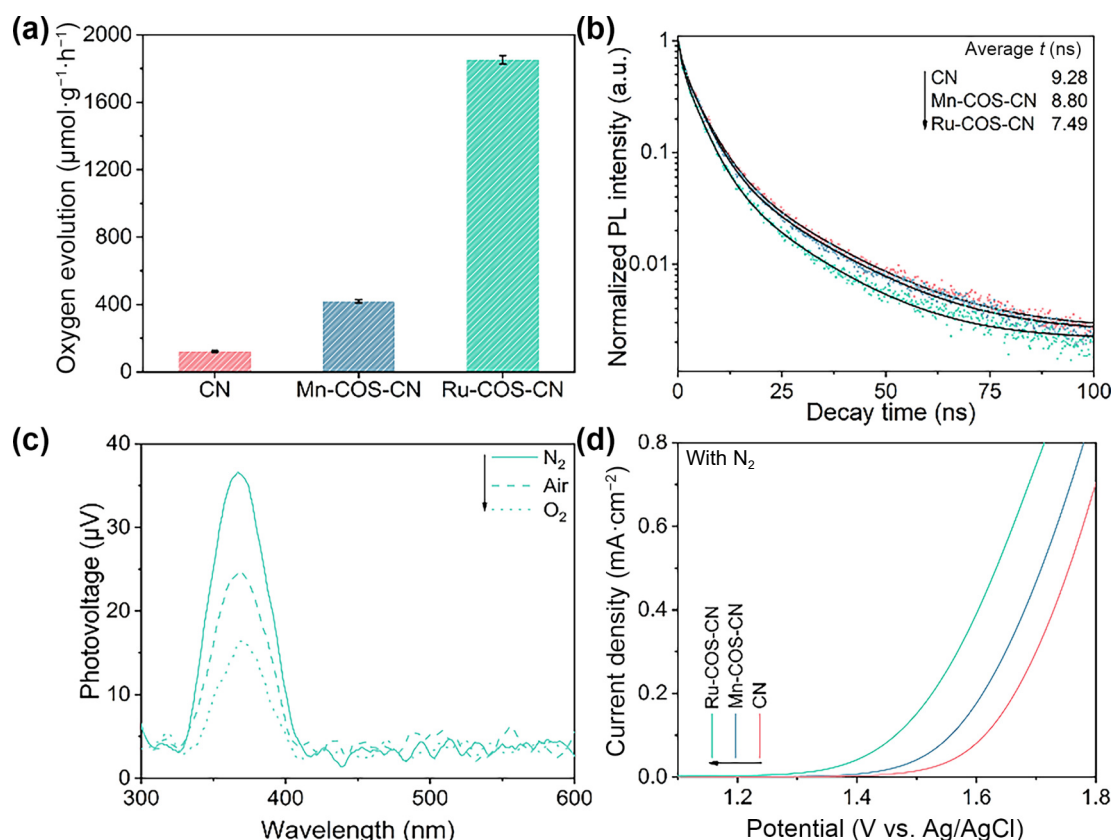


Figure 3 Performance of oxygen evolution reaction and the roles of Ru-Oxo in charge modulation. (a) Photoactivities of oxygen evolution reaction of CN, Mn-COS-CN, and Ru-COS-CN. The error bars (mean $\pm$ standard deviation) were obtained based on three independent photocatalytic experiments. (b) TR-PL spectra of CN, Mn-COS-CN, and Ru-COS-CN. (c) AC-SPS of Ru-COS-CN. (d) Electrochemical oxidation curves of CN, Mn-COS-CN, and Ru-COS-CN samples in the N_2 -bubbled system.

S12(g) and S12(h) in the ESM, RuO₂-CN treatment results in average fresh and dry weight increases of 33.5% and 29.5%, respectively, relative to the CK, although these rates are lower than those observed for Ru-COS-CN. This outcome further supports the positive correlation between plant growth promotion and water oxidation performance of the photocatalysts.

3.4 Mechanism for tobacco growth promotion

To better understand the mechanism underlying tobacco growth promotion following Ru-COS-CN treatment, chlorophyll was extracted at day 20 after the Ru-COS-CN treatment to explore the effect of the photocatalyst on chlorophyll synthesis. As a vital photosynthetic pigment, chlorophyll plays an essential role in capturing light energy for photosynthesis. Elevated chlorophyll content typically enhances solar radiation absorption, thereby increasing photosynthetic potential and promoting plant growth [38–40]. As shown in Fig. S13(a) in the ESM, the content of chlorophyll is almost no variation after foliar application of CN, Mn-COS-CN, and Ru-COS-CN, indicating that improved photosynthesis stems from factors other than chlorophyll content. Furthermore, the influence of chitosan, Mn²⁺, and Ru³⁺ on tobacco growth was studied. As shown in Fig. S13(b) in the ESM, these individual components had no substantial impact on fresh weight, dry weight, plant length, or leaf area, confirming that the observed growth promotion was mainly attributed to the photocatalysts sprayed on the tobacco leaves rather than the influence of chitosan and metal ions. Moreover, as indicated by PL spectra (Fig. S10(a) in the ESM), the luminescence intensity of CN gradually decreased after the modification of Mn-Oxo and Ru-Oxo clusters. This evidence supports that the enhancement in tobacco growth is not related to the luminescence of CN, but is likely associated with the improved water oxidation performance of the photocatalysts.

Transient absorption spectroscopy (TAS) plays an essential role

in understanding the charge carrier dynamics of photocatalysts. This technique utilizes a pump-probe setup with a pulse laser as the excitation light and a tungsten-halogen lamp as probe light, allowing the capture of photogenerated transient species through the observation of their relaxation over time [14, 41]. In this study, μ s-TAS was employed to investigate the charge transfer and catalytic mechanism of the photocatalysts, as the μ s-timescale is directly relevant to the photocatalytic process. To examine the charge carrier kinetics of CN, Mn-COS-CN, and Ru-COS-CN, μ s-TAS was conducted by mimicking the reaction conditions. As shown in Fig. 4(a), Mn-COS-CN exhibited an extended half-life (26.3 μ s) relative to CN (11.6 μ s), while Ru-COS-CN showed a much longer half-life of 43.9 μ s under N₂, indicating that M-Oxo clusters facilitate the capture of photogenerated holes, enhancing charge separation and prolonging the half-life time of photogenerated electrons. This hole capture effect by Ru-Oxo aligns with the SPS responses observed in Fig. 3(c). Furthermore, in N₂ (g) containing H₂O (N₂ (H₂O)), the half-life times of Mn-COS-CN and Ru-COS-CN were extended to 38.1 and 65.3 μ s, respectively (Fig. S14 in the ESM). This is likely due to the activation of H₂O further facilitating charge separation, thus prolonging the half-life time of photoelectrons. As the capturing of photogenerated electrons by O₂, the half-life time for Mn-COS-CN and Ru-COS-CN in air was decreased compared to that in the N₂ (H₂O), yet remained longer than that under N₂ condition (Fig. 4(b)). Such a prolonged half-life time of photogenerated electrons induced by the boosted water oxidation process will undoubtedly be conducive to their transfer from photocatalysts to the tobacco, potentially contributing to the observed promotion in tobacco growth.

To verify whether the enhanced photosynthetic activity was attributed to the transfer of electrons generated by the water oxidation of photocatalysts to chloroplasts, the Hill reaction was conducted using 2,6-dichlorophenolindophenol (DCPIP) as an

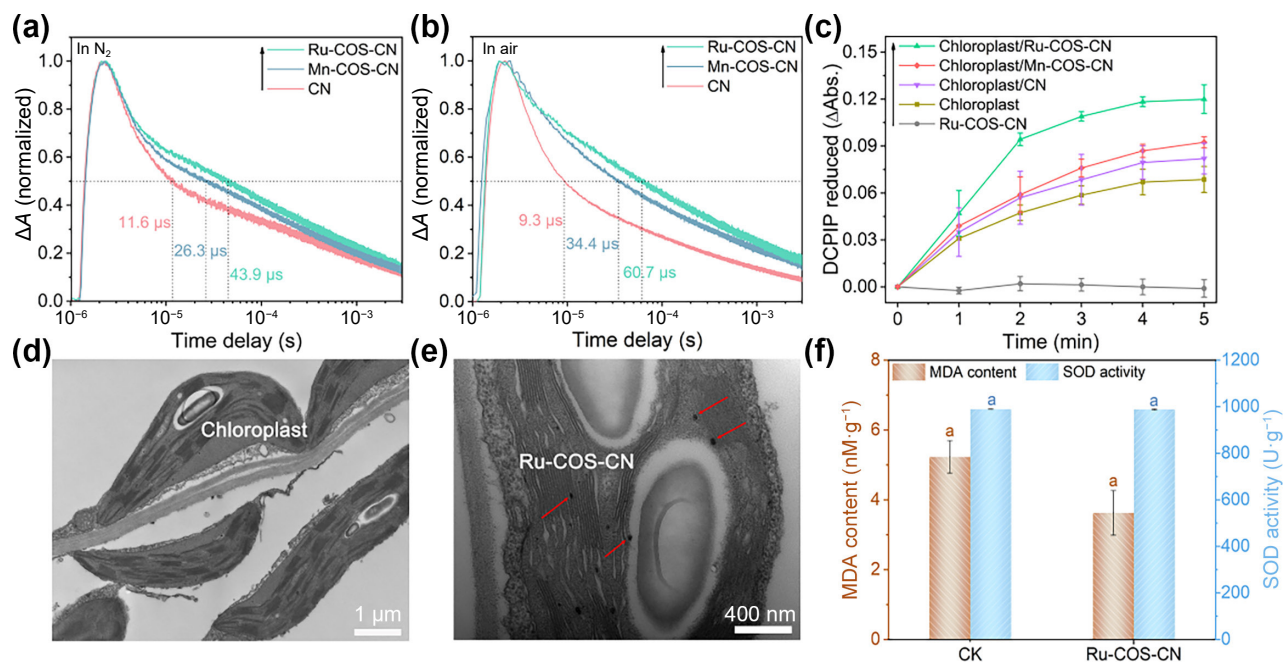


Figure 4 Measurement of charge carrier dynamics and photosynthetic activity. μ s-TAS decay kinetics of CN, Mn-COS-CN, and Ru-COS-CN monitored at 900 nm, (a) in N₂ and (b) in air. (c) DCPIP reduction in Ru-COS-CN, chloroplast, chloroplast/CN complexes, chloroplast/Mn-COS-CN complexes, and chloroplast/Ru-COS-CN complexes, respectively, light intensity: 20 mW·cm⁻², photocatalyst: 100 mg·L⁻¹. (d) TEM image of Ru-COS-CN nanosheets sprayed tobacco leaf cells. (e) TEM image of Ru-COS-CN nanosheets in chloroplast of tobacco leaf cell. (f) MDA content and SOD activity of tobacco with and without Ru-COS-CN treatment. The values are presented as mean $\pm$ SD. Significant differences among treatments are indicated with different letters.

artificial electron acceptor, which has a high affinity for electrons transferred from PS II to photosystem I (PS I) during the photoreaction [42–44]. As shown in Fig. 4(c), Ru-COS-CN was unable to reduce the DCPIP in the absence of chloroplasts, confirming that only the photogenerated electrons, which arise from the water oxidation of Ru-COS-CN and are subsequently captured by chloroplasts, contribute to the reduction of DCPIP. The results show that chloroplasts with CN exhibited greater DCPIP reduction than chloroplasts alone, with further enhancement observed in the chloroplast/Mn-COS-CN complex. The maximum reduction of DCPIP was achieved with the chloroplast/Ru-COS-CN complex. These findings indicate that the photogenerated electron from Ru-COS-CN is effectively transferred to chloroplasts, facilitating DCPIP reduction and consequently enhancing the photosynthetic activity of tobacco. Then, the distribution of Ru-COS-CN nanosheets in the tobacco leaves was investigated by TEM. As illustrated in Figs. 4(d) and 4(e), it was clearly seen that the smaller Ru-COS-CN nanosheets entered the cell and located in the tobacco chloroplasts. However, the structure and morphology of tobacco cells had no obvious change upon exposure to Ru-COS-CN nanosheets. Meanwhile, the distribution of Ru-COS-CN on tobacco leaves was conducted during the first 5-day interval of foliar application (Fig. S15(c) in the ESM). The decrease in fluorescence intensity further indicated potential internalization of the catalyst into the leaf cells.

Previous studies have shown that engineering nanomaterials typically induce oxidative stress in plants by producing reactive oxygen species (ROS) [45, 46]. To evaluate the potential phytotoxicity of Ru-COS-CN nanosheets on tobacco, the malondialdehyde (MDA) content and superoxide dismutase (SOD) activity in tobacco were measured at day 20 after foliar application of Ru-COS-CN suspension. MDA is one of the products of lipid peroxidation in cell membrane, which often occurs in plant organs during aging or under adverse environmental conditions, serving as an indicator of membrane lipid peroxidation and plant stress response [47, 48]. Higher MDA levels typically reflect lower stress resistance. As shown in Fig. 4(f), there was no obvious difference in MDA content with and without Ru-COS-CN treatment, demonstrating that the photocatalyst had unnoticeable influence on the tobacco cytomembrane. SOD is an enzyme involved in the decomposition of superoxide anion radicals ($\cdot\text{O}_2^-$) in plants through the reaction $2\cdot\text{O}_2^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$. Hydrogen peroxide (H_2O_2) is subsequently broken down into water and oxygen by catalase, preventing the oxidative damage of macromolecules, cellular structures, and functions due to $\cdot\text{O}_2^-$. SOD activity is thus a key physiological marker of plant stress resistance [49]. The results in Fig. 4(f) show that SOD activity in tobacco leaves treated with Ru-COS-CN nanosheets did not significantly differ from the control. Both MDA content and SOD activity exhibited no obvious changes, indicating that Ru-COS-CN nanosheets do not exhibit phytotoxic effects on tobacco.

Based on these findings, a schematic mechanism for the observed promotion of tobacco growth by Ru-COS-CN treatment is proposed, as shown in Fig. 5(a). When Ru-COS-CN nanosheets are sprayed onto the tobacco leaves, they evenly distribute on the leaf surface due to their strong interaction with the leaves. A portion of smaller nanosheets will penetrate the tobacco cells and enter the chloroplasts. Under light irradiation, particularly ultraviolet exposure, the Ru-COS-CN nanosheets were excited, generating electron-hole pairs. The photogenerated holes in the valence band

(VB) of CN would be rapidly extracted by the anchored Ru-Oxo clusters, which enhances charge separation and accelerates the water oxidation process, thereby generating long-lived photogenerated electrons. These electrons are subsequently transferred to the chloroplasts of tobacco, enhancing the ETR within the ETC, which promotes photosynthetic efficiency and ultimately results in enhanced tobacco growth.

To examine the broader applicability of this approach, boron-doped CN (BCN) and Ru-Oxo cluster-anchored BCN (Ru-COS-BCN), with enhanced thermodynamic driving force for water oxidation, were successfully fabricated and foliar spraying for promoting tobacco growth. The XRD pattern of Ru-COS-BCN shows characteristic diffraction peaks at 13.1° and 27.3° , corresponding to the (100) and (002) planes of CN (Fig. S16(a) in the ESM). UV-vis absorption spectrum further indicates that the Ru species modification did not change the optical absorption properties of BCN (Fig. S16(b) in the ESM). As can be observed from Fig. S16(c) in the ESM, TEM image reveals a 2D structure of Ru-COS-BCN, and the energy-dispersive X-ray spectroscopy mapping of Ru-COS-BCN demonstrates the successful loading of B and Ru species with uniform distribution (Fig. S16(d) in the ESM). The transient state surface photovoltage (TS-SPV) spectra were obtained to further elucidate the role of Ru species in CN and BCN. As shown in Fig. S17 in the ESM, almost no TS-SPV signal was observed for CN, while Ru-COS-CN exhibited a clear negative response. A reduced signal can be observed for BCN after decoration with Ru species. These results firmly verified that Ru species could effectively capture the photogenerated hole, improving charge transfer and separation, consistent with SPS results shown in Fig. 3(c).

The photocurrent response of Ru-COS-BCN is higher than that of BCN alone, indicating enhanced charge separation (Fig. S18(a) in the ESM). The photogenerated carrier dynamics of BCN and Ru-COS-BCN were further investigated by μs -TAS. It can be seen from Fig. S18(b) in the ESM that under N_2 conditions, Ru-COS-BCN exhibited an extended half-life of photogenerated electrons (58.2 μs) compared to BCN (16.4 μs). Under N_2 (H_2O) conditions, the electron half-life further increased to 74.1 μs for Ru-COS-BCN and to 18.7 μs for BCN (Fig. S18(c) in the ESM), indicating that water activation further prolongs electron lifetime. In an air atmosphere, the half-life times were reduced to 14.9 μs for BCN and 68.7 μs for Ru-COS-BCN (Fig. S18(d) in the ESM), which is in good agreement with the phenomenon observed for Ru-COS-CN. Compared to Ru-COS-CN, this further enhanced water oxidation activity and the extended half-life of photogenerated electrons will be more conducive to promoting tobacco growth.

Subsequently, the effects of BCN and Ru-COS-BCN on tobacco growth were systematically evaluated. As shown in Figs. 5(b) and 5(c), foliar spraying of BCN and Ru-COS-BCN nanosheets effectively promoted tobacco growth, with average increase in fresh weight and dry weight of 15.7% and 13.6% for BCN, respectively, and 51.7% and 41.8% for Ru-COS-BCN. Notably, a positive correlation was observed between the average increase ratios in fresh and dry weights for treatments with CN, BCN, Ru-COS-CN, and Ru-COS-BCN and their photocatalytic water oxidation performance (Figs. 5(d) and 5(e) and Fig. S19 in the ESM). These findings suggest that the promotion is attributed to the production of long-lifetime photoelectrons resulting from the extended utilization of sunlight and the accelerated photocatalytic water oxidation, as well as to the efficient transfer of electrons to the

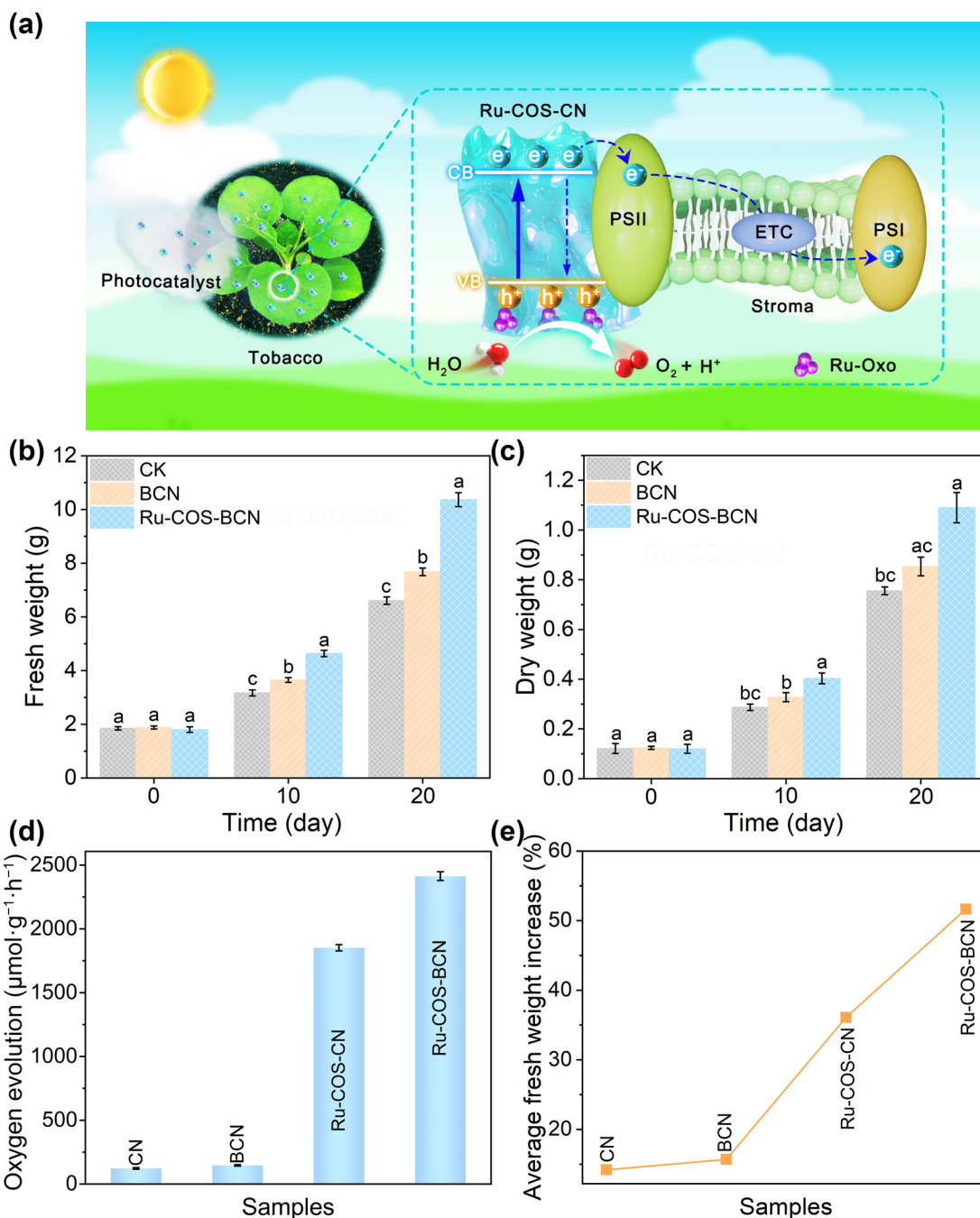


Figure 5 Mechanism for tobacco growth promotion and applicability of photocatalysts. (a) Illustration of enhanced photosynthetic activity of tobacco. (b) Fresh weight and (c) dry weight of tobacco treated with BCN and Ru-COS-BCN. The error bars (mean $\pm$ standard deviation) were obtained based on three independent photocatalytic experiments. (d) Photoactivities of oxygen evolution reaction for CN, BCN, Ru-COS-CN, and Ru-COS-BCN. (e) Average fresh weight increase ratios of tobacco after foliar spraying with CN, BCN, Ru-COS-CN, and Ru-COS-BCN. The values are presented as mean $\pm$ SD. Significant differences among treatments are indicated with different letters.

chloroplasts with an enhancing ETR in the ETC. This process leads to increased photosynthetic activity and promoted tobacco growth.

4 Conclusions

In summary, this study has shown that the tobacco growth was largely promoted after foliar spraying of photocatalysts, which exhibited a positive correlation with their water oxidation performance, and the tobacco treated by Ru-COS-CN nanosheets exhibits the most prominent enhancement, with average fresh

weight, dry weight, plant length, and leaf area increasing by 36.1%, 36.8%, 27.4%, and 15.9% per 10 days, respectively. The *in situ* μ -transient absorption spectra demonstrated that the long-lifetime photoelectrons are generated through the improved utilization of sunlight and an accelerated water oxidation process. These photoelectrons are subsequently transferred to the chloroplasts with an enhanced ETR in the ETC, thereby promoting tobacco growth. This study offers a promising approach for promoting plant growth by elaborate photocatalysts with improved utilization of sunlight

and accelerated water oxidation performance, paving the way for the development of sustainable agricultural technologies to improve crop yields.

Electronic Supplementary Material: Supplementary material (spectroscopic and materials characterization data, including XRD patterns, XPS analysis, TEM image, AFM image, UV-vis spectra, μ s-TAS, TS-SPV responses, water oxidation performance, evaluation of charge separation, contact angle test, phenotype and fluorescence photographs of tobacco, fresh weight and dry weight of tobacco, chlorophyll contents analysis, surface temperature curves and thermal images of tobacco, Figs. S1–S19, and Table S1) is available in the online version of this article at <https://doi.org/10.26599/NR.2025.94907498>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

G. W. W.: Data curation, validation, experimental design, writing manuscript. K. H.: Data curation, validation, experimental design. J. Q. L.: Data curation. Z. J. L.: Morphology characterization. Y. Q., B. Y., and Y. G. W.: Methodology. Z. Q. Z., Z. L., and H. Y. L.: Project administration, experimental design, revising manuscript. L. Q. J.: Project administration, project design, funding acquisition, revising manuscript. All authors contributed to the manuscript preparation.

Use of AI statement

None.

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