

Particulate organic matter triggers photoelectrotrophic denitrification: An overlooked biogeochemical reaction induced by sunlight

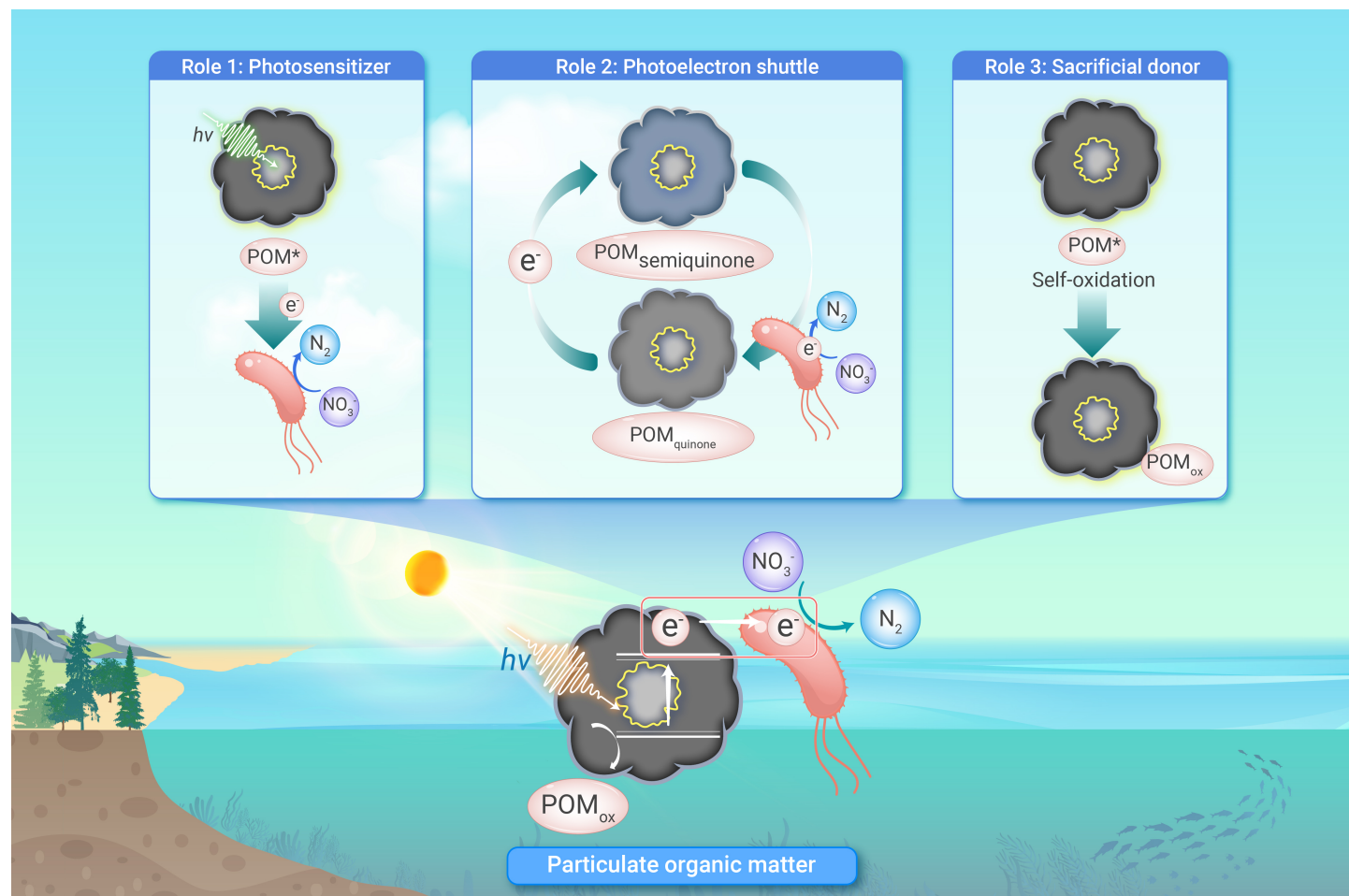
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GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- Particulate organic matter (POM) can trigger photoelectrotrophic denitrification (PEDeN).
- POM promotes PEDeN by acting as a bacterial photosensitizer, photoelectron shuttle and sacrifice agent.
- POM with self-oxidation during triggering PEDeN may impact carbon turnover in ecosystems.
- Highlights overlooked biogeochemical processes of elements/pollutants driven by POM-microbe systems.

Particulate organic matter triggers photoelectrotrophic denitrification: An overlooked biogeochemical reaction induced by sunlight

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Particulate organic matter (POM) is a major carbon pool in terrestrial and aquatic ecosystems and its biogeochemical processes significantly affect the global carbon cycle and trophic levels of ecosystems. As a natural photosensitizer, there have been no reports on photoelectron transfer from POM to microorganisms, leading to the long-term neglect of POM biogeochemical processes. Using photoelectrotrophic denitrification (PEDeN) as a model system, this study is the first to demonstrate the POM-triggered PEDeN effect; that is, photoelectrons from POM were used to drive microbial denitrification. By constructing the *Thiobacillus denitrificans*-POM system, it was found that irradiation accelerated nitrate reduction with a kinetic constant of $0.03 \pm 0.007 \text{ h}^{-1}$. Irradiation resulted in a complete denitrification with nitrogen as the main product ($56.3 \pm 8.8\%$), compared to the dark system with nitrite as the main product. The significantly upregulated ($p < 0.01$) denitrifying genes support the idea that the conversion of nitrate to nitrogen is a microbial-mediated process. During this process, POM plays multiple roles: photosensitizing microorganisms, mediating photoelectron transfer, and acting as a sacrificial donor. The first two roles of POM have not been established previously, revealing a new electron-transfer mechanism between POM and microorganisms. The latter accelerated POM dissolution, representing a newly discovered POM photodissolution process involving microorganisms. The study highlights the previously overlooked photoelectrochemical reactions of POM with microorganism, emphasizing the need to explore the biogeochemical processes triggered by POM-microorganisms system and suggesting a strategy for promoting sunlight-driven denitrification in surface environments.

INTRODUCTION

Photoelectrotrophic denitrification (PEDeN) has emerged as a novel type of denitrification and has garnered significant attention in recent years.^{1,2} PEDeN is a process in which denitrifying microorganisms use photoexcited electrons from a photosensitizer to reduce nitrate (NO_3^-)/nitrite (NO_2^-) to the gaseous nitrogenous products, rather than relying on traditional organic or inorganic substrates as electron donors.^{3,4} This unique process enables the removal of NO_3^- solely through irradiation without the need for additional chemical or electric energy consumption, highlighting the potential of PEDeN as an economically viable and sustainable technology for NO_3^- removal.^{5,6} Furthermore, this process presents an opportunity to recover high-purity nitrous oxide (N_2O), a potent oxidant, from NO_3^- -containing wastewater.⁷ Beyond its innovative applications in wastewater treatment and energy recovery, PEDeN offers new insights into the natural nitrogen cycle, particularly regarding the pathway by which nitrogen returns to the atmosphere.⁸ The environmental significance of PEDeN has motivated further exploration of its natural occurrence.

Recently, dissolved organic matter (DOM), a natural photosensitizer, has been shown to directly transfer photoexcited electrons to denitrifiers for NO_3^- reduction upon irradiation.⁹ This indicated the potential occurrence of PEDeN in natural ecosystems. Compared to DOM, particulate organic matter (POM), another type of natural organic matter (NOM), constitutes a significant portion of the carbon pool in ecosystems.^{10,11} POM exists widely in aqueous water and is major component of soil organic matter (SOM).¹² It is estimated that POM comprises >50% of SOM and >70% of that in the lithified sediment.¹³ Similar to DOM, POM exhibits photoactive properties.¹⁴ When irradiated, POM is photoexcited to its excited state (POM^*), which can trans-

fer photoelectrons to the surrounding electron acceptors, such as oxygen (O_2).¹⁵ This process generates reactive oxygen species (ROS), which play a role in the conversion of environmental elements and pollutants.¹⁴⁻¹⁶ Superoxide radicals generated by POM irradiation promoted the reduction of silver ions (Ag^+) to silver nanoparticles (AgNPs). The contribution of POM to the formation of natural AgNPs is estimated to be 11-31%, highlighting the significant role of POM in influencing the biogeochemical cycling of contaminants.¹⁶

Despite its widely recognized photosensitivity, current studies have primarily focused on the photoelectron transfer from POM to abiotic compounds.^{15,16} The understanding of the electron exchange between POM and bacteria is limited to the electron shuttle function of POM in the dark.¹⁷ POM, also known as humin, is bioinert, but chemically active.¹⁸ It acts as an electron shuttle to accelerate microbial extracellular electron transfer,¹⁹ such as Fe(III) oxide reduction,²⁰ 2, 4, 6-trichlorophenol dehalogenation²¹ and NO_3^- reduction.²² Additionally, POM has been utilized to promote direct interspecies electron transfer (DIET) processes, suggesting its role as an electron acceptor and donor for microorganisms.^{19,23} However, there are no reports on photoelectron transfer from POM to bacteria. There is still uncertainty regarding whether irradiation, an important factor in ecosystems, influences the electron transfer process between POM and bacteria.

POM is assumed to exhibit chemical features similar to those of DOM.²⁴ However, there are significant differences between POM and DOM. POM is more insoluble than DOM. The heterogeneous nature of POM allows it to easily adsorb contaminants and gather microorganisms,²⁵ creating a microecological environment that acts as a reaction center. Aggregates formed by POM, microorganisms, and contaminants provide a spatial advantage for electron transfer among them.²⁵ Moreover, it allows microorganisms to compete effectively with O_2 for photo-induced electrons.^{8,25} Given the significant POM reservoirs, the effects of the POM-triggered PEDeN process in the natural environment may be considerable. Revealing this effect holds promise for a comprehensive understanding of the pathways through which nitrogen returns to the atmosphere in terrestrial and aquatic ecosystems, with implications for soil fertility, N_2O emissions, and water quality. Moreover, as POM is often considered bioinert,²⁵ this finding offers new insights into the biogeochemical processes of POM that play important roles in ecosystem trophic levels and global carbon cycles. Importantly, POM in soil and sediment plays a crucial role in mediating electron transfer,¹⁷ which supports anaerobic microbial respiration. The discovery of a photoelectrotrophic relationship between POM and bacteria suggests a previously overlooked process that significantly affects the electron-mediating capacity of soil and sediment. These findings indicate the environmental significance of the photoelectrotrophic processes triggered by POM.

The aim of this study is to demonstrate the occurrence of the POM-triggered PEDeN effect and reveal the multiple roles of POM during this process. POM samples were extracted from the coastal mangrove sediment. A *Thiobacillus denitrificans*-POM (*T. denitrificans*-POM) system was constructed to investigate the occurrence of PEDeN. *T. denitrificans* was used as the model denitrifier, offering distinct advantages due to its nonphototrophic and strictly autotrophic nature, and eliminating confounding phototrophic and heterotrophic processes during irradiation.²⁶ Moreover, its capability to absorb photoexcited electrons for NO_3^- reduction further underscores its suitability for this study.³ The denitrification process, resulting nitrogenous products, and the relative transcription abundance of the denitri-

fying genes by *T. denitrificans*-POM during irradiation were analyzed. The multiple roles of POM in photosensitizing denitrifiers, mediating photoelectron transfer, and serving as a sacrificial donor in PEDeN were examined. The results of this study unveil a new relationship between POM and microorganisms, and provide insights into the biogeochemical nature of NO_3^- and POM in sunlit ecosystems.

MATERIALS AND METHODS

Extraction and characterization of POM

POM was extracted from a sediment of coastal mangrove in Zhangzhou province, China (23°95' N, 117°33' E). The sediment samples were first dried at 25 °C, sieved through a 2 mm sieve, and then stored at -20 °C for further analysis. The POM extraction steps were based on a previous study and are described as follows. The sediment sample (500 g) was progressively extracted with 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$ eight times, 0.1 M NaOH seven times, and 0.2 M NaOH ten times with an extractant/soil ratio of 10:1. The suspension was stirred for 24 h and centrifuged at 4500 $\times$ g for 20 min. The precipitate was washed with Milli-Q water, freeze-dried, and ground to pass through a 100 mesh (0.15 mm) sieve. The ash was further treated with 1.6 M HCl/3 M HF at an extractant/soil ratio of 10:1 for 24 h; this process was repeated six times.^{16,27}

Characterization of POM

The morphology of the POM was analyzed using field-emission transmission electron microscopy (FETEM, Talos F200S G2, Thermo Fisher Scientific, MA, USA). The absorption spectrum of the POM suspensions was recorded using an ultraviolet-visible (UV-vis) spectrophotometer equipped with an integrating sphere (UV-2600, Shimadzu, Kyoto, Japan).³ All the electrochemical measurements were performed using a CHI760E electrochemical workstation (Chenhua Inc., Shanghai, China). The I-t curves of POM were recorded by constructing a three-electrode system, in which a POM-coated glassy carbon (GC) electrode was the working electrode, a Pt plate (0.5 cm $\times$ 0.5 cm) was the counter electrode and a saturated calomel electrode (SCE) was the reference electrode. During the I-t curve determination, the applied potential was setup at 0.3 V (vs. SCE).⁹ The electron exchange capacity of POM was also determined using a three-electrode system, in which a graphite plate (2 cm $\times$ 2 cm) replaced the GC electrode as the working electrode. For electron accepting capacity (EAC) and electron donating capacity (EDC) measurement, the potential was set at -0.73 V and +0.37 V (vs. SCE), respectively. Methylviologen (MV^{2+}) (0.1 mL, 10 mM) and 2, 2'-azino-bis (3-ethyl-benzothiazoline-6-sulfonic acid) (ABTS) (0.1 mL, 10 mM) were added as the electron shuttle. Following the stabilization of the background current, 0.2 mL of a deoxygenated POM suspension (236 mgC L⁻¹) was repeatedly added to the solution for EAC or EDC determination.²⁸

Construction and characterization of *T. denitrificans*-POM

T. denitrificans (DSM 12475) was purchased from the Leibniz Institute DSMZ, German Collection of Microorganisms and Cell Cultures. *T. denitrificans* was cultured in Medium 113 (Table S1) as described in our previous study.³ When the OD₆₀₀ of the medium was approximately 0.2, the suspension was centrifuged, washed, and suspended in a 120 mL anaerobic serum bottle, which contained 20 mL of modified Medium 113 (Table S1). The *T. denitrificans*-POM was constructed by directly adding 1 mL degassed POM solution to the above *T. denitrificans* suspension, and the POM concentration was maintained at 10 mgC L⁻¹. The morphology of the *T. denitrificans*-POM was characterized using field-emission scanning electron microscopy (FESEM, TESCAN MIRA LMS, Brno, Czech Republic) and FETEM. Additionally, the composition of surface elements of the *T. denitrificans*-POM system was analyzed using an energy dispersive X-ray spectroscopy (EDS).

PEDeN process driven by *T. denitrificans*-POM

Before irradiation, a dose of KNO_3 solution (NO_3^- , 2.5 mg/L) was injected into the *T. denitrificans*-POM bottles, then the bottles were deoxygenized via alternately (four times) evacuating the air in the headspace (0.1 kPa, 30 min) and filling up with high-purity helium (99.999%, 120 kPa, 1 min). The irradiation of the bottle was performed using a light-emitting diode (LED) array

composing 395 $\pm$ 5 nm LEDs (0.5-10.0 mW cm⁻²). The experimental group (*T. denitrificans*-POM (light)) and controls (*T. denitrificans*-POM (dark), POM (light), POM (dark), *T. denitrificans* (light) and *T. denitrificans* (dark)) were established. Samples were collected using disposable sterile syringes (1 mL) and filtered using 0.22 μ m membranes for nitrogenous products determination. All experiments were performed at 30°C and each experiment had three replicates. To investigate the generation of N_2 during irradiation, bottles were injected with a dose of C_2H_2 (10%, v/v) to inhibit nitrous oxide reductase activity.⁹

To demonstrate the direct photoelectron transfer between POM and bacteria, a biophotoelectrochemical cell was constructed as previously described.⁹ The cathode was *T. denitrificans* biofilm-coated ITO, whereas the anode was PBS (0.1 M, pH = 7) containing 10 mg C L⁻¹ POM. The anode was irradiated using the LED, and the NO_3^- concentration at the cathode (kept out of light) was measured over time. To analyze the photodissolution process of POM, the solutions from anode before and after each reaction were collected, and then their components were measured using excitation-emission matrix fluorescence spectroscopy (G9800A, Agilent, CA, USA). The procedures and parameters for the fluorescence measurements were obtained from a previous work.⁹

H_2O_2 treatment of POM

To investigate the effect of the electron shuttle on the PEDeN process, POM was subjected to hydrogen peroxide (H_2O_2) oxidation to eliminate quinone functions.²⁹ POM oxidation was performed by adding 25 mL of 30% H_2O_2 to 0.5 g of POM. The solution was stirred for 15 h, followed by heat treatment at 90 °C for 45 mins, then washing with distilled water, and freeze-drying. The H_2O_2 -treated POM was denoted as POM H_2O_2 . The photocurrent of POM H_2O_2 was determined using the method described in the text.

Semiquinone-type radicals of POM determined by using electron spin resonance

Electron spin resonance (ESR) spectra of the POM were acquired at ambient temperature using an ESR spectrometer (A300-10/12, Bruker, Ettlingen, Germany) at 9.4 GHz with 100 kHz modulation of the steady magnetic field.^{16,19} The detailed parameters were as follow: a magnetic field centered at 336.4 mT, 0.998 mW microwave power, 30 s sweep period, and 0.03 s time constant. To determine the effect of irradiation on the ESR signal of POM, capillary tubes containing the POM suspension were illuminated for 0 min, 5 min and 20 min using a lamp at 395 nm or 520 nm (PFS-5050P60A-12).

Measurements of photoluminescence spectra and luminescence decay curves

The fluorescence spectrum of the POM was determined using an FLS980 fluorescence spectrometer, and the maximum excitation (E_{ex}) and emission (E_{em}) wavelengths were assured. The photoluminescence (PL) decay curves were measured using an FLS980 fluorescence spectrometer, employing a nanosecond hydrogen lamp as the excitation light source.

Analytical methods

The NO_3^- concentration was determined by using ion chromatography (ICS 900, Dionex, Thermo Fisher Scientific). Analysis of nitrogenous products, including NO_2^- -N, during denitrification was conducted using the ICS system.^{3,30} The N_2O -N concentrations and CO_2 concentrations were determined by the GC (Agilent 7890), where the gas concentrations were determined by using an electron capture detector and a thermal conductivity detector.^{9,31} Excitation-emission matrix (EEM) fluorescence spectroscopy was used to analyze the components of DOM produced by POM photodissolution by a fluorescence spectrophotometer (G9800A, Agilent, U.K.). Fluorescence region integral (FRI) analysis was used to quantify the DOM content, and MATLAB R2014a software was employed for processing the EEM data.⁹ The relative transcription abundances of denitrifying genes in *T. denitrificans*-POM (light), *T. denitrificans*-POM (dark), and *T. denitrificans* (light) were quantified using reverse transcription-quantitative polymerase chain reaction (RT-qPCR), as previously described.³ Three replicate amplifications were performed in all experiments.

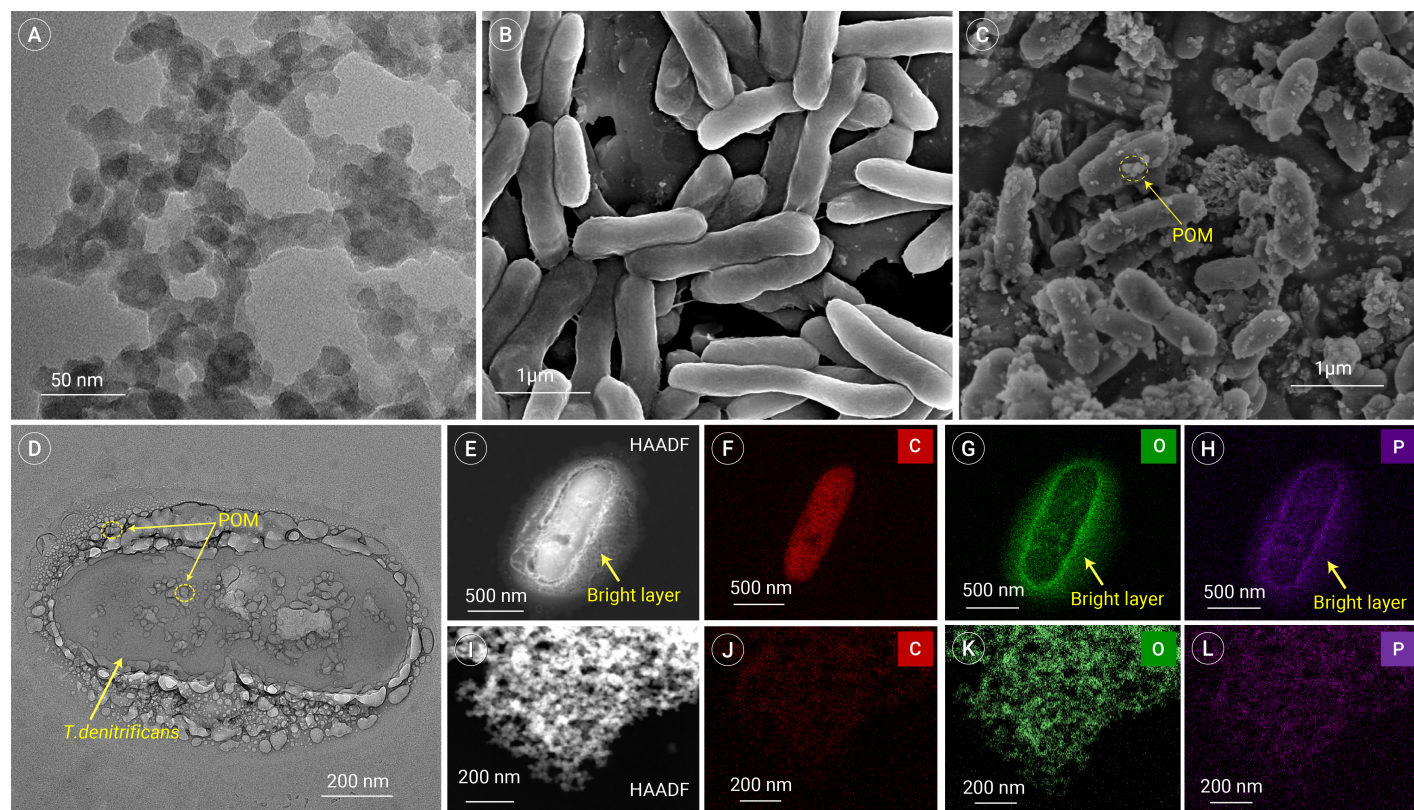


Figure 1. Characterization of POM, *T. denitrificans* and *T. denitrificans*-POM system (A) TEM image of POM. (B, C) SEM images of *T. denitrificans* and *T. denitrificans*-POM system. (D) TEM image of *T. denitrificans*-POM system. High-angle annular dark field (HAADF) images of *T. denitrificans*-POM system (E) and POM (I), and the EDS mapping images of C, O, and P of *T. denitrificans*-POM system (F-H) and POM (J-L).

RESULTS AND DISCUSSION

Construction and characterization of *T. denitrificans*-POM system

The *T. denitrificans*-POM system was constructed by directly mixing POM (10 mgC L^{-1}) with a *T. denitrificans* ($\text{OD}_{600} = 0.2$) suspension. The TEM images of pure POM showed that the size of the POM ranged from 20 nm to 100 nm (Figure 1A). After mixing with POM, obvious particle-coated bacteria were observed, compared to bare *T. denitrificans*, which had a smooth surface (Figures 1B-C). TEM images of *T. denitrificans*-POM revealed particle enfoldment around the bacteria (Figure 1D). To further demonstrate the spatial relationship between POM and bacteria, high-angle annular dark field (HAADF) and elemental mapping images of *T. denitrificans*-POM and POM were collected (Figures 1E-L). HAADF images of *T. denitrificans*-POM showed a bright bacterial surface, suggesting a coating on the bacteria (Figure 1E). Although the bacterial compositions resembled those of POM, distinct differences in the C, O, and P percentages were observed (Table S2). EDS revealed that the percentages of C, O, and P in *T. denitrificans* and POM were 86.0%, 13.6%, and 0.2% and 73.0%, 21.4%, and 3.9%, respectively (Table S2). POM had a lower percentage of C and higher percentages of O and P than that of *T. denitrificans*. The higher ratio of O and P in POM than in *T. denitrificans* resulted in a bright bacterial surface in the O and P mapping images (Figures 1G-H & K-L) in the *T. denitrificans*-POM system, whereas no such phenomenon was observed in the C mapping image (Figures 1F & J). Moreover, the percentages of C, O, and P in the *T. denitrificans*-POM hybrid were 76.9%, 19.6%, and 3.4%, respectively, which were between those of POM and *T. denitrificans* (Table S2), further demonstrating that POM was enfolded around the bacteria. These results indicated the successful construction of the *T. denitrificans*-POM system. Because POM is a complex material, hydrophilic and hydrophobic components are present in POM.³² A more comprehensive coverage of TEM images showed that the *T. denitrificans*-POM was surrounded by a separation shell (Figure S1), which might be the hydrophobic components in POM. Therefore, the binding force that enables POM to spontaneously combine with bacteria might be due to the hydrophilic domains of POM. FTIR spectrum of POM also demonstrated that

POM had abundant hydrophilic functional groups such as hydroxyl and carboxyl groups (Figure S2). These groups have the potential to form the binding force with the surface of bacteria.

POM-triggered PEDeN process

To explore the possibility of POM-triggered PEDeN process, a series of deletional control experiments were constructed. As shown in Figure 2A, a faster NO_3^- reduction is observed in *T. denitrificans*-POM (light) than in the controls. The reduction of NO_3^- in *T. denitrificans*-POM (light) followed a pseudo-first-order reaction ($R^2 = 0.99$) with a kinetic constant of $0.03 \pm 0.007 \text{ h}^{-1}$, whereas the rate constants of NO_3^- reduction in *T. denitrificans*-POM (dark), *T. denitrificans* (light) and POM (light) were $0.01 \pm 0.00 \text{ h}^{-1}$, $0.00 \pm 0.00 \text{ h}^{-1}$ and $0.00 \pm 0.00 \text{ h}^{-1}$, respectively (Figure S3). The results demonstrated that irradiation accelerated NO_3^- reduction in the *T. denitrificans*-POM system. The NO_3^- reduction in *T. denitrificans*-POM (dark) was due to reductive functional groups (e.g., hydroquinone), which acted as electron donors for anaerobic respiration.³³ Because no NO_3^- was reduced in POM (light), it indicated that the NO_3^- reduction by *T. denitrificans*-POM was a microorganism-mediated process.

Analysis of nitrogenous products showed that no NO_2^- -N was detected in *T. denitrificans*-POM (light), where a mass of NO_2^- -N accumulated in *T. denitrificans*-POM (dark), and the percentage of NO_2^- -N in the nitrogenous products was 100% (Table S3). N_2O -N detection was exclusive to *T. denitrificans*-POM (light), constituting $32.6 \pm 7.6\%$ of nitrogenous products (Table S3). To confirm N_2 production, the acetylene inhibition technique was used. Figure 2B shows that more N_2O is produced after C_2H_2 addition in *T. denitrificans*-POM (light), indicating N_2O conversion to N_2 . The N_2 -N percentage in nitrogenous products was $56.3 \pm 8.8\%$, affirming N_2 as the dominant product in *T. denitrificans*-POM (light). In contrast, almost no N_2O was detected in *T. denitrificans*-POM (dark) with or without C_2H_2 , further demonstrating that NO_2^- was not reduced to N_2O or N_2 (Figure 2B). These differential products in *T. denitrificans*-POM (light) and *T. denitrificans*-POM (dark) indicate that irradiation induced a complete denitrification process. This phenomenon has also been

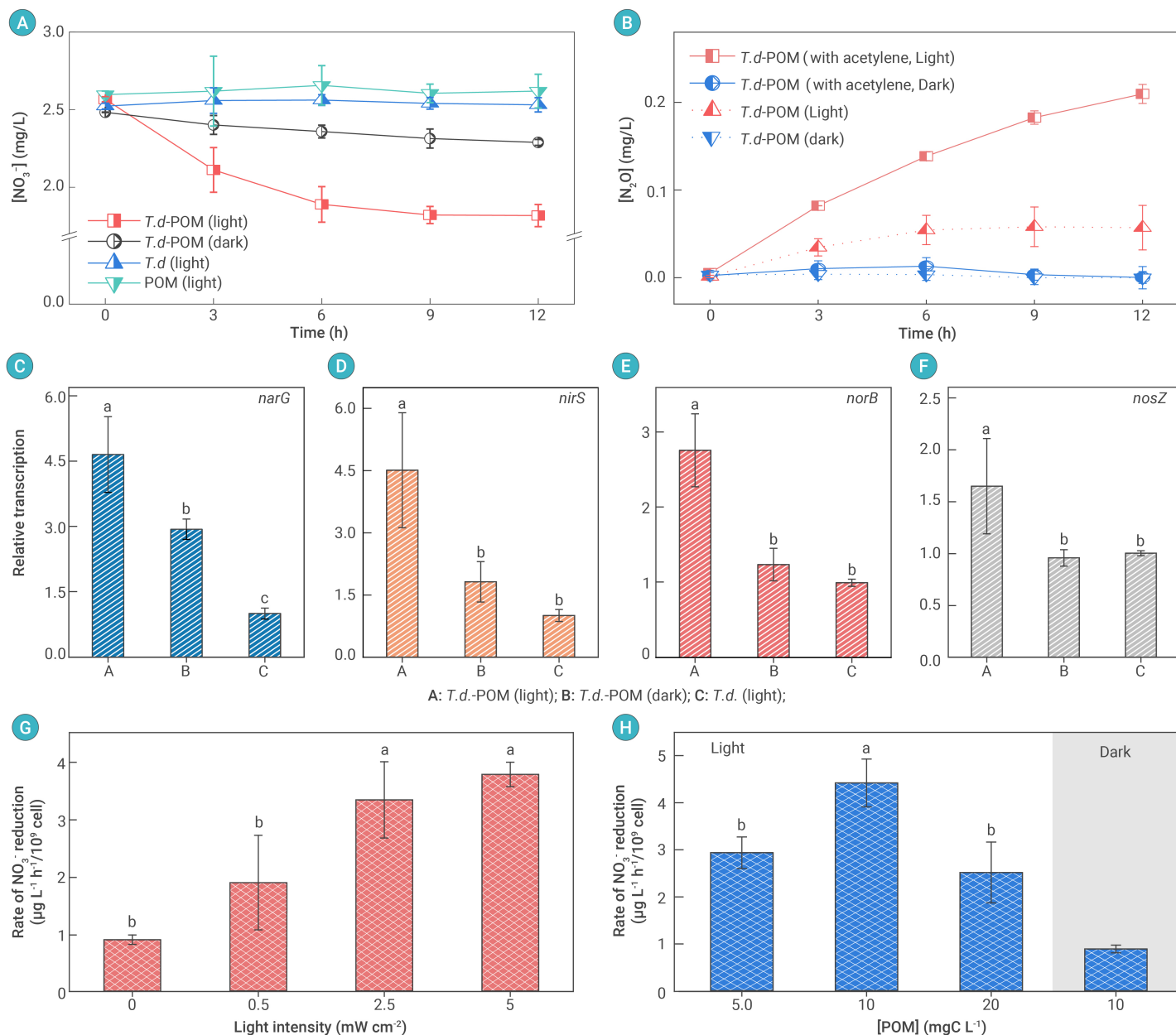


Figure 2. PEDeN process by *T. denitrificans*-POM (A) Time curves of NO_3^- reduction by *T. denitrificans*-POM and control experiments under 395 ± 5 nm light irradiation. The reactions were performed in serum bottles. The cell concentration was 8.98×10^9 cell mL^{-1} . (B) Time curves of N_2O production with and without 10% C_2H_2 as nitrous oxide reductase inhibitor. (C-F) Relative transcription abundance of the denitrifying genes *narG*, *nirS*, *norB* and *nosZ* in *T. denitrificans*-POM (light), *T. denitrificans*-DOM (dark) and *T. denitrificans* (light) after 12 h of reaction. (G, H) Effects of light intensity (G) and POM concentration (H) on the rate of NO_3^- reduction by *T. denitrificans*-POM (light). Separate letters indicate statistically significant differences at $p < 0.05$.

reported in *T. denitrificans*-DOM⁹ and periphytic biofilm-TiO₂ systems.³⁴ Without irradiation, NO_2^- accumulates because of a lack of electron donors. Upon irradiation, it generates more electrons for the denitrifier and induces the expression of the photoelectron uptake pathway, promoting the further reduction of NO_2^- to N_2 in the periplasmic space.³⁵

RT-PCR experiments further demonstrated that NO_3^- was reduced to N_2 by *T. denitrificans*-POM (light). The microbial denitrification process consists of four steps ($\text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$), involving nitrate reductase (Nar), nitrite reductase (Nir), nitric oxide reductase (Nor), and nitrous oxide (Nos).³⁶ Figures 2C–F shows that the expression of the *nar*, *nir*, *nor*, and *nos* genes in *T. denitrificans*-POM (light) after 12 h of reaction, was significantly ($p < 0.01$) upregulated by 4.7 ± 0.9 -fold, 4.5 ± 1.3 -fold, 2.8 ± 0.5 -fold and 1.6 ± 0.4 -fold, respectively, in comparison with *T. denitrificans* (light). In *T. denitrificans*-POM (dark), only *nar* expression was significantly ($p < 0.05$) upregulated, where the expression of the *nir*, *nor*, and *nos* genes did not differ significantly from that of *T. denitrificans* (light). These results indicated that denitrifying

gene expression was consistent with the denitrification process observed in *T. denitrificans*-POM (light) and *T. denitrificans*-POM (dark).

The POM-triggered PEDeN process is affected by light intensity and POM concentration ([POM]). The rate of NO_3^- reduction by *T. denitrificans*-POM (light) significantly increased from 1.9 ± 0.8 $\mu\text{g L}^{-1} \text{h}^{-1}/10^9$ cell to 3.8 ± 0.2 $\mu\text{g L}^{-1} \text{h}^{-1}/10^9$ cell as the light intensity increased from 0.5 mW cm^{-2} to 5.0 mW cm^{-2} (Figure 2G). Elevated light intensity promotes stronger photoelectrochemical reactions of POM, thereby generating more photoelectrons. This is demonstrated by the I-t curves, in which the maximum photocurrent of the POM increases with increasing light intensity (Figure S4A). Conversely, with [POM] changing from 5.0 to 20.0 mgC L^{-1} , its rate of NO_3^- reduction first increased from 2.9 ± 0.4 $\mu\text{g L}^{-1} \text{h}^{-1}/10^9$ cell to 4.4 ± 0.5 $\mu\text{g L}^{-1} \text{h}^{-1}/10^9$ cell, then decreased to 2.5 ± 0.6 $\mu\text{g L}^{-1} \text{h}^{-1}/10^9$ cell (Figure 2H). Notably, the rate of NO_3^- reduction tended to saturate at 10 mgC L^{-1} POM. High [POM] induce the coagulation of POM, decreasing its photosensitivity. An obvious precipitate was observed when [POM] was higher than 20 mgC L^{-1} . Additionally,

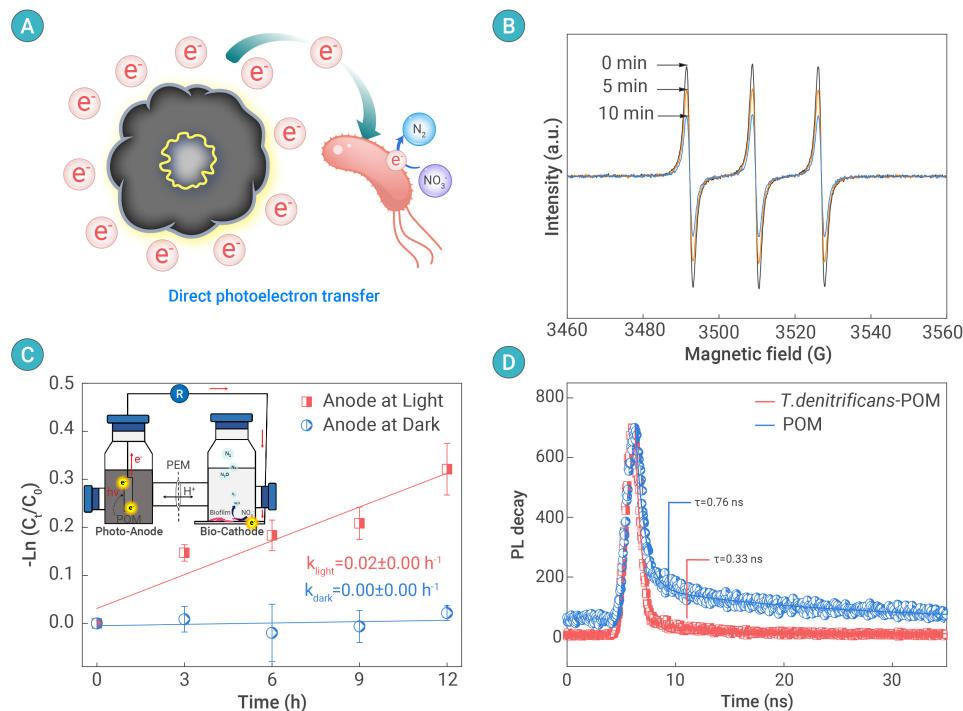


Figure 3. Evidence lines of POM as bacterial photosensitizer (A) Schematic diagram of POM as a bacteria's photosensitizer via direct photoelectron transfer. (B) ESR spectra of POM aqueous solution containing TEMPO as spin probe before irradiation, after 5 min of irradiation and 10 min of irradiation. (C) Plotting of time curves of NO₃⁻ reduction using pseudo-first-order kinetics. The inset is the configuration of biophotoelectrochemical cell. (D) PL decay curves of *T. denitrificans*-POM and POM. The excitation and emission wavelengths were 401 nm and 430 nm, respectively.

ingredients in POM decreased with time, resulting in the attenuation of photocurrent. This trend is consistent with previous observations on DOM.⁹

To demonstrate direct photoelectron transfer from POM to *T. denitrificans*, the photoreductive ability of POM and photoelectron transfer from POM to denitrifiers were assessed (Figure 3A). The ESR spectra were obtained using a POM solution containing TEMPO as the spin probe. TEMPO is a spinning tag molecule with a stable triplet ESR spectrum of magnitude 1:1:1. The signal flattened upon the reaction of TEMPO with reducing agents (H⁺/e⁻) in an inert atmosphere.³⁷ Figure 3B shows that

the ESR signal intensity of TEMPO gradually decreases with irradiation time, indicating TEMPO reduction by POM irradiation and thus demonstrating the photoreduction ability of POM.³⁷ The photoreduction ability of POM induces the generation of reactive oxygen species (ROS) through direct photoelectron transfer from POM to O₂.¹⁵

Direct photoelectron transfer from the POM to the denitrifier was verified by constructing a dual-chamber biophotoelectrochemical cell (Figure S7). In the cell, POM acted as the photoanode and *T. denitrificans* biofilm served as the biocathode. This setup prevented POM interference by acting as an electron donor for *T. denitrificans* in the dark. Irradiating the anode chamber allowed the photoelectrons generated from POM to be transferred to the cathode via an external circuit, which were finally accepted by the *T. denitrificans* biofilm for NO₃⁻ reduction. As shown in Figure 3C, NO₃⁻ is reduced under light conditions with a kinetic constant of 0.02 ± 0.00 h⁻¹, whereas the NO₃⁻ concentration in dark conditions does not significantly change. This strongly suggests that the photoelectrons produced from POM were taken up by *T. denitrificans*. Furthermore, the PL decay curves provide additional evidence of photoelectron transfer from POM to microorganisms. Upon mixing *T. denitrificans* with POM, the fluorescence intensity in *T. denitrificans*-POM decayed markedly faster than in pure POM, resulting in a decreased lifetime of transient absorption of POM from 0.76 ns to 0.33 ns (Figure 3D). This was due to the presence of more available proximal electron acceptors in *T. denitrificans*, indicating that photoelectrons were taken up by the denitrifier. A similar phenomenon was observed in the CdS-sensitized *T. denitrificans* system, in which the fluorescence lifetime decreased from 9.71 ns to 1.08 ns.³⁵ The larger decrease in the fluorescence lifetime in the CdS-based system than in the POM-based system suggests that photoelectron transfer from CdS to *T. denitrificans* is more efficient than that from POM to *T. denitrificans*. This is because the biologically induced photosensitized system (*T. denitrificans*-CdS) created a more efficient photoelectron transfer pathway than the autodeposition system (*T. denitrificans*-POM).

Multiple roles of POM in triggering PEDeN

Because POM is a complex material, it may play several roles in triggering PEDeN. First, irradiation significantly enhanced denitrification by *T. denitrificans*. This is a result of the photosensitivity of the POM. Therefore, POM may directly photosensitize denitrifiers to provide additional electron sources (photoelectrons). Second, POM is an electron shuttle because of the presence of quinone groups. Quinone groups can accelerate photoelectron transfer and enhance photoelectron utilization by denitrifiers. However, the use of POM as a photoelectron shuttle has rarely been reported. Third, because no sacrificial reagent is added, POM also acts as an end-electron source for the system. To reveal the denitrification mechanism in the *T. denitrificans*-POM system, the multiple roles of POM as a bacterial photosensitizer, photoelectron shuttle, and sacrificial agent were clearly understood.

Direct photoelectron transfer from POM to denitrifier (photosensitizer)

The UV-vis spectrum of POM demonstrated that the POM had a wide absorption range from 250–800 nm (Figure S5) owing to the presence of abundant chromophorous groups in POM.¹⁶ However, the light absorption of the functional groups was overlapping, resulting in no significant characteristic peak in the absorption spectra of POM. The I-t curve also showed the excellent photoresponse properties of POM (Figure S6). The photoelectric conversion property of POM played a basic role in inducing light-driven microbial denitrification process. During irradiation of POM, the photocurrent of POM decreased with time. It was because that self-oxidation of POM occurred in absence of external sacrificial reagent. Therefore, the oxidizable

the ESR signal intensity of TEMPO gradually decreases with irradiation time, indicating TEMPO reduction by POM irradiation and thus demonstrating the photoreduction ability of POM.³⁷ The photoreduction ability of POM induces the generation of reactive oxygen species (ROS) through direct photoelectron transfer from POM to O₂.¹⁵

Direct photoelectron transfer from the POM to the denitrifier was verified by constructing a dual-chamber biophotoelectrochemical cell (Figure S7). In the cell, POM acted as the photoanode and *T. denitrificans* biofilm served as the biocathode. This setup prevented POM interference by acting as an electron donor for *T. denitrificans* in the dark. Irradiating the anode chamber allowed the photoelectrons generated from POM to be transferred to the cathode via an external circuit, which were finally accepted by the *T. denitrificans* biofilm for NO₃⁻ reduction. As shown in Figure 3C, NO₃⁻ is reduced under light conditions with a kinetic constant of 0.02 ± 0.00 h⁻¹, whereas the NO₃⁻ concentration in dark conditions does not significantly change. This strongly suggests that the photoelectrons produced from POM were taken up by *T. denitrificans*. Furthermore, the PL decay curves provide additional evidence of photoelectron transfer from POM to microorganisms. Upon mixing *T. denitrificans* with POM, the fluorescence intensity in *T. denitrificans*-POM decayed markedly faster than in pure POM, resulting in a decreased lifetime of transient absorption of POM from 0.76 ns to 0.33 ns (Figure 3D). This was due to the presence of more available proximal electron acceptors in *T. denitrificans*, indicating that photoelectrons were taken up by the denitrifier. A similar phenomenon was observed in the CdS-sensitized *T. denitrificans* system, in which the fluorescence lifetime decreased from 9.71 ns to 1.08 ns.³⁵ The larger decrease in the fluorescence lifetime in the CdS-based system than in the POM-based system suggests that photoelectron transfer from CdS to *T. denitrificans* is more efficient than that from POM to *T. denitrificans*. This is because the biologically induced photosensitized system (*T. denitrificans*-CdS) created a more efficient photoelectron transfer pathway than the autodeposition system (*T. denitrificans*-POM).

Mediating photoelectron transfer from POM to denitrifier (photoelectron shuttle)

The transformation of quinones into reductive quinones (semiquinones) is a typical characteristic of electron shuttles.³⁸ To demonstrate the role of POM as a photoelectron shuttle in mediating photoelectron transfer (Figure 4A), ESR spectroscopy was used to evaluate the involvement of the quinone moieties in POM during irradiation. The ESR signal at g = 2.0036, a characteristic of semiquinone, increased with irradiation time, suggesting that the

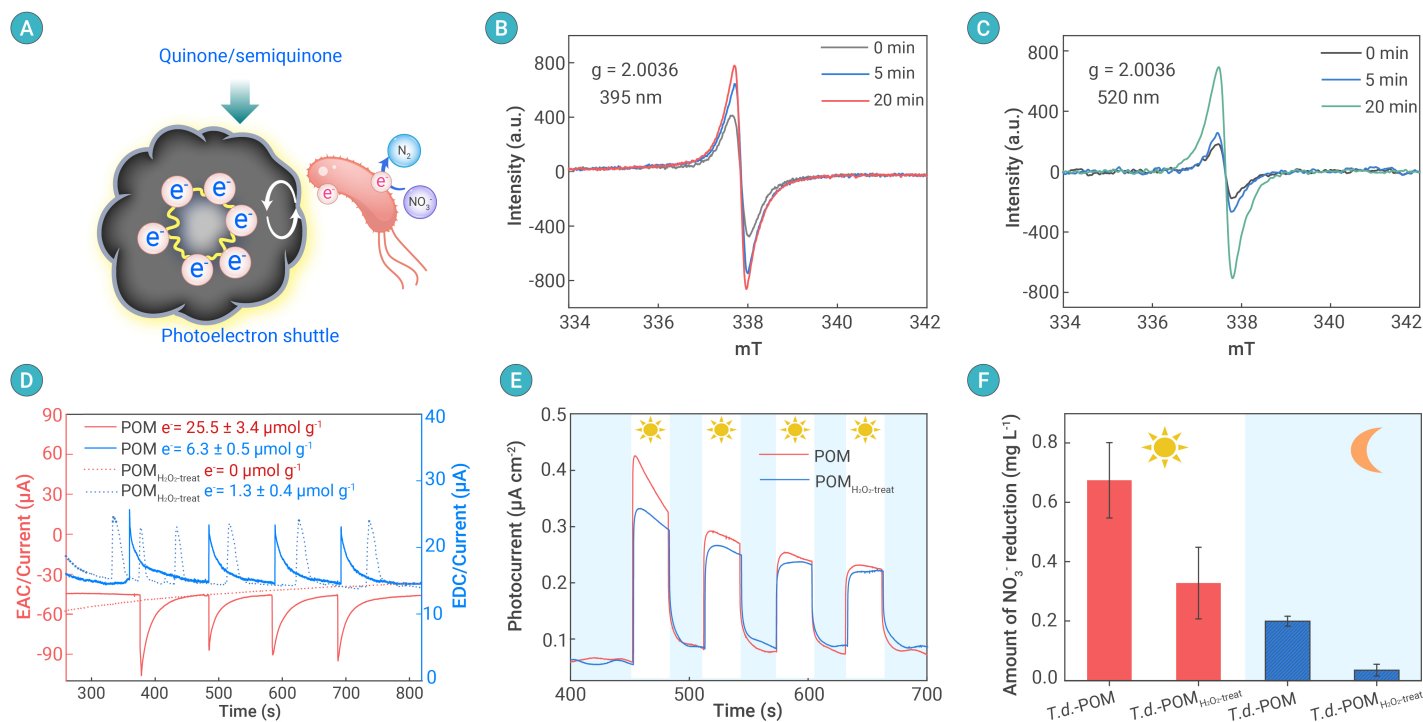


Figure 4. Evidence lines of POM as photoelectron shuttle during PEDeN process (A) Schematic diagram of POM as an electron shuttle for photoelectron shuttle. ESR spectra of semiquinone radical in POM solution after 0, 5 and 20 min irradiation with 395 nm (B) and 520 nm lamp (C). (D) EDC/EAC measurements of POM and H₂O₂-treated POM. (E) I-t curves of POM and H₂O₂-treated POM. The concentration of POM and H₂O₂-treated POM were equal. (F) Effects of H₂O₂-treated POM (48 h) on amount of NO₃⁻ reduction.

generation of semiquinone was induced by irradiation (395 nm) (Figure 4B).³⁹ Semiquinones can arise from the direct photoexcitation of quinones⁷ or from the intramolecular photoelectron transfer from other chromophore groups, such as phenol groups, to quinones. To demonstrate the occurrence of intramolecular photoelectron transfer, a wavelength of 520 nm was used as the light source to exclude the direct photoexcitation of the quinone groups because the excitation wavelength of quinones is typically <450 nm.⁴⁰ However, the generation of semiquinone upon irradiation was also observed (Figure 4C). These results suggest that the intramolecular photoelectron transfer process in POM irradiation involves quinone groups; that is quinone acts as a photoelectron shuttle.

To further investigate the influence of the electron-shuttling role of POM on the PEDeN effect, the electron-shuttling ability of POM was eliminated by H₂O₂ oxidation.²⁹ The ability of the original POM to mediate electron transfer was characterized by quantifying its EDC and EAC. The average EAC of POM was $25.5 \pm 3.4 \mu\text{mol g}^{-1}$, whereas the average EDC of POM was $6.3 \pm 0.5 \mu\text{mol g}^{-1}$ (Figure 4D). After treatment with H₂O₂, the EAC and EDC of POM_{H₂O₂-treat} decreased to $0 \mu\text{mol g}^{-1}$ and $1.3 \pm 0.4 \mu\text{mol g}^{-1}$ (Figure 4D), respectively, indicating that the ability of electron shuttle of POM was almost eliminated. The H₂O₂-treated POM did not significantly alter the photocurrent, based on the I-t curves of the POM and POM_{H₂O₂-treat} (Figure 4E). However, when H₂O₂-treated POM replaced original POM, a significant decrease in the amount of NO₃⁻ reduction (0.35 mg L^{-1} , 12 h) was observed in *T. denitrificans*-POM_{H₂O₂-treat} (light) (Figure 4F). Similarly, the amount of NO₃⁻ reduction by the hybrid at dark also decreased from 0.20 to 0.03 mg L⁻¹ after H₂O₂ treatment of POM. This reduction was attributed to the near elimination of the reductive electrons in POM by H₂O₂ oxidation. However, the H₂O₂ treatment could not completely eliminate the electron-donating capacity of POM (the EDC value of POM_{H₂O₂-treat} was $1.3 \pm 0.4 \mu\text{mol g}^{-1}$), resulting in that the *T. denitrificans*-POM_{H₂O₂-treat} (dark) was still able to reduce NO₃⁻. This phenomenon was also observed in the previous study; it was found that the H₂O₂ treatment of humin could still act as electron donor for microbial reductive pentachlorophenol.²⁹ Notably, the higher amplitude of the decreased amount of NO₃⁻ reduction by *T. denitrificans*-POM under light conditions (0.35 mg L^{-1}) than dark conditions (0.17 mg L^{-1}) suggested the positive role of electron shuttle in POM to mediate photoelectron PEDeN. During POM-driven PEDeN, both photoelec-

trons and reductive electrons were the electron sources for *T. denitrificans*. After treatment with H₂O₂, the contribution of photoelectrons significantly increased from 69.8% to 89.7%, while that of the reducing electrons significantly decreased from 30.2% to 10.3% (Figure S8). The enhanced contribution of photoelectrons was due to the removal of reducing functional groups by H₂O₂ treatment.

Semiquinones can mediate NO₃⁻ reduction via microbial oxidation.⁷ Therefore, the light-induced semiquinone of POM can directly transfer electrons to bacteria for NO₃⁻ reduction. However, as an additional advantage of the kinetics of direct photoelectron transfer,⁷ photoelectrons on the surface of POM are preferred for direct transfer to bacteria, rather than for quinone/semiquinone transformation. In contrast, in the POM subsurface, the quinone/semiquinone transformation can accelerate photoelectron transfer from POM to the denitrifier. This results in a greater reduction in the amount of NO₃⁻ in the presence of quinone moieties in light than in the dark.

POM acted as an end-electron source (sacrificial reagent)

NOMs can be used as a sacrificial donor in photocatalytic systems.⁴¹ In *T. denitrificans*-POM (light), POM did not undergo mineralization, as no more CO₂ was detected after 12 h of reaction (Figure S9). However, the photoelectrotrophic reaction between POM and microorganisms enhanced the photodissolution of POM, as evidenced by fluorescence analysis of the supernatant. A stronger fluorescence signal was observed in *T. denitrificans*-POM (light) than in *T. denitrificans*-POM (dark) or POM (light) (Figures 5A–D), indicating more DOM generation. This was due to the presence of bacteria, which can take up photoelectrons, thereby facilitating charge separation of the photoexcited POM and promoting its self-oxidation. This phenomenon has also been observed in the DOM driven PEDeN processes.⁹ In the DOM-triggered PEDeN process, DOM has been demonstrated to serve as an end-electron donor for denitrifiers, resulting in an intramolecular redox reaction and greater removal of redox moieties in DOM.⁹ Similarly, the change in POM during the PEDeN process mainly involved the conversion of redox moieties rather than POM mineralization. This resulted in the photodissolution of POM into DOM. This is a new POM photodissolution mechanism, in which the presence of bacteria promotes the photodissolution of POM. To determine the photolysis ratio of POM to DOM, the volume integrals of DOM based on

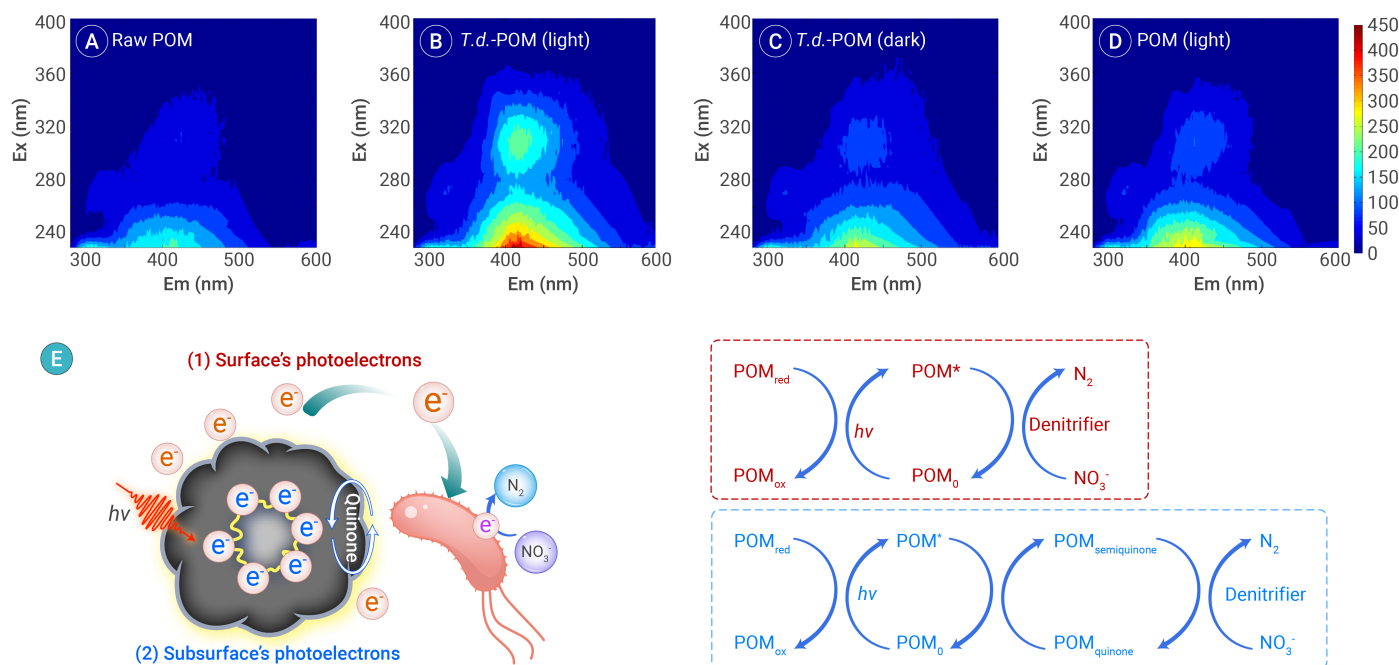


Figure 5. Three-dimensional fluorescence spectra (EEM) of (A) Raw, (B) *T. denitrificans*-POM (light), (C) *T. denitrificans*-POM (dark) and (D) POM (light) after reaction Excitation wavelength: 230~450 nm; Step size: 10 nm; Emission wavelength: 280~600 nm; Step size: 2 nm. (E) Proposed mechanism in POM triggered PEDeN. POM_{red} indicates the POM in reductive state and POM_{ox} indicates the POM in oxidative state; POM₀ indicates the ground state of POM and POM* indicates the excited POM; POM_{semiquinone} and POM_{quinone} indicates the quinone moieties state in POM.

the three-dimensional fluorescence data were calculated (Figure S10). It was found that there was no significant difference between POM (light) and raw POM, indicating that no significant POM photolysis to DOM happened. In the anaerobic condition (lacking of electron acceptor), the charge was difficult to be separated and the ROS was difficult to form, therefore, the photolysis of POM was greatly inhibited. Nevertheless, the volume integral value of DOM in *T. d.*-POM (light) increased to 2.3 time after 12 h reaction, in comparison to that of raw POM, suggesting a significant photolysis of POM to DOM in *T. d.*-POM (light). The presence of bacteria will promote the charge separation and self-oxidation of POM. These results further support that the photodissolution process of POM can be accelerated by the interaction of light and microorganisms, especially under anaerobic condition. Because POM is the primary carbon pool on Earth, even small changes in its behavior can impact global carbon cycling. The DOM generated from POM can be further converted into CO₂ by microorganisms, affecting the carbon budget.

Possible mechanisms of POM-triggered PEDeN

Because of the possibility of DOM photosensitizing denitrifiers,⁹ the dissolved POM after irradiation was mixed with *T. denitrificans*. However, after 12 h of irradiation, there was no change in the NO₃⁻ concentration (Figure S11), indicating that the photodissolved ingredient from POM did not drive PEDeN. This may be because the concentration of the photodissolved ingredients was too low to drive the PEDeN process. Therefore, POM played a primary role in triggering PEDeN. Based on the above results, a possible mechanism for POM-triggered PEDeN is proposed (Figure 5E). When POM comes in contact with the denitrifier, it spontaneously adsorbs onto the surface of the microorganism. Upon exposure to sunlight, ground-state POM (POM₀) is excited to POM*, which directly releases photoelectrons to the denitrifier or indirectly transfers them to the bacteria via quinone/semiquinone transformation. The presence of quinone moieties in POM accelerates photoelectron transfer from POM to the denitrifier. Photoelectrons promote the photoelectron transfer pathway, which may involve the expression of membrane-bound proteins (e.g., cytochrome *c*₄) to promote the reduction of NO₃⁻ to N₂ catalyzed by a series of denitrifying enzymes.³⁵ The denitrification rate can be enhanced by increasing the [POM] or light intensity. In contrast, the presence of PEDeN promotes charge separation of POM* and self-oxidation of POM, resulting in increased DOM generation from the photodissolution of POM.¹⁴

CONCLUSIONS

This study provides the first evidence that POM triggers the PEDeN process. Irradiation significantly increased NO₃⁻ reduction and induced a complete denitrification process with N₂ as the major product. The rates of NO₃⁻ reduction in the POM-based PEDeN systems were comparable to those in the DOM-based systems. The significant upregulation of denitrifying genes supports the notion that the conversion of NO₃⁻ to N₂ is a microbial-mediated process. During this process, POM plays multiple roles: photosensitizing microorganisms, mediating photoelectron transfer, and acting as a sacrificial donor. The first two roles of POM have not been established previously, and reveal a novel light-induced electron transfer process between POM and microorganisms. The discovery of the photoelectrotrophic relationship of POM with microorganisms provides insight into the biogeochemistry of NO₃⁻ and POM, and reveals an underappreciated electron-mediated capacity in soil and sediment. However, further studies are required to verify the presence of POM-triggered PEDeN in complex environments. In another way, because POM is low cost and widespread, optimizing the effect can be applied to an economic denitrification technology for practical wastewater. In summary, the study sheds light on the previously overlooked photoelectrochemical reaction of POM with microorganisms, and highlights the importance of biogeochemical processes of element/pollutants triggered by the POM-microbial systems and suggests a strategy for light-driven denitrification in surface environments.

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AUTHOR CONTRIBUTIONS

M. Chen conceived, organized, and revised the manuscript. S. F. Huang conducted experiments, created figures, and drafted the manuscript. J. X. Luo and Y. M. Diao assisted in the extraction of POM and characterization of POM. D. Zhang, R. J. X. Zeng and S. G. Zhou performed editing and language revision of the manuscript. All authors reviewed the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

All data are available in the main text or the supplementary materials.

SUPPLEMENTAL INFORMATION

It can be found online at <https://doi.org/10.59717/j.xinn-geo.2024.100129>

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