CoWO$_{4-x}$-Based Photothermal Membranes for Solar-Driven Water Evaporation and Eutrophic Lake Water Purification

Haixia Liu, Chunyu Yang, Wei Guo,*, Feng Zhang, Huiming Lin, Le Zhao, Tianyue Ma, Xinxin Lu,* and Fengyu Qu*

Cite This: ACS Omega 2020, 5, 31598–31607

ABSTRACT: Solar-driven water evaporation has been proven to be a promising and efficient method for the energy crisis and clean water shortage issues. Herein, we strategically design and fabricate a novel nonstoichiometric CoWO$_{4-x}$ deposited foam nickel (NF) membrane (CoWO$_{4-x}$@NF) that possesses all the desirable optical, thermal, and wetting properties for efficient water evaporation and purification. The broadband absorption of CoWO$_{4-x}$ nanoparticles (NPs) obtained by hydrogen reduction contributes to light-to-heat conversion, while NF with a three-dimensional porous structure can support CoWO$_{4-x}$ NPs and ensure the rapid flow of water molecules during the water evaporation process. We systematically explore and compare the outdoor water evaporation performance of the pure water group, NF group, and CoWO$_{4-x}$@NF group, and the results show that CoWO$_{4-x}$@NF performs well under natural sunlight irradiation (water evaporation: 2.91 kg m$^{-2}$ h$^{-1}$). Significantly, under solar irradiation, the remarkable reduction of Cyanophyta and Euglenophyta in lake water is achieved in the CoWO$_{4-x}$@NF membrane-administered group, and these two algae are the main factors for eutrophication of the lake water. Our work highlights the great potentials of the CoWO$_{4-x}$@NF membrane as a device for realizing outdoor solar energy-driven water evaporation and proposes a new strategy for purifying the eutrophication of the lake water.

INTRODUCTION

Because energy crisis and clean water shortage can lead to economic failure, environmental degradation, harsh human survival conditions, and possibly even wars, numerous scientists are committed to solving these two critical issues.$^1$–$^6$ Solar energy is abundant and clean energy, and solar-driven water evaporation has been considered as a low-cost, environmentally friendly, and highly efficient way of addressing the above issues.$^7,^8$ Solar-driven water evaporation can utilize seawater, polluted rivers or lakes, and domestic wastewater to achieve clean water, which can solve the problems of complex treatment processes, high energy consumption, and high costs in traditional treatment methods.$^9$ An effective strategy for water evaporation is to localize heat at the air–water interface by depositing an absorber on a porous support, which can efficiently absorb solar irradiation and convert it to heat energy.$^{10}$ To date, various novel materials have been proposed as light-absorbing agents in the water evaporation field, including carbon-based nanomaterials, plasmonic metal particles, black metal oxides, semimetallic nanoparticles, and organic polymers.$^{11}$–$^{20}$ Among them, some kinds of non-stoichiometric compounds (e.g., WO$_x$N, MoO$_{3-x}$, and TiO$_x$) have aroused great interest in scientists, mainly because they have strong photoabsorption characteristics in a wide range of wavelengths, so they are more suitable for converting solar energy to thermal energy to generate steam power.$^{21}$ CoWO$_{4-x}$ NPs, as one of the nonstoichiometric compounds, have a full spectral absorption in the range of 450–2500 nm because of the band gap absorption. Besides, the CoWO$_{4-x}$ NPs also have the advantages of a low cost, high production yield, and simplified fabrication process,$^{22}$ which have been identified as a potential candidate for solar energy harvesting.

Foam nickel (NF), a foamlike material made of metallic nickel, has a high specific surface area, sound absorption coefficient, and excellent thermal/electrical conductivity, so it is commonly used for battery electrode materials, catalyst materials, and sound-absorbing materials.$^{23}$ In 2017, Yang et al. developed a centimeter-scale BiInSe$_3$-coated NF (BiInSe$_3$@NF) for solar energy-driven water evaporation for the first time. The results showed that the BiInSe$_3$@NF membrane displayed a high evaporation rate of 0.83 kg m$^{-2}$ h$^{-1}$ under 1 sun irradiation, which was 2.5 times that of pure water.$^{24}$ Besides, there are also some examples of water evaporation...
using NF as a support such as Co$_3$O$_4$@NF, SnSe@NF, Ni-NiO$_x$@NF, porous rGO@NF, and L-TiO$_2$@NF. From the above studies, it can be found that there are still some essential challenges that need to be solved for photothermal membranes based on NF: (i) multiple complicated membrane preparation processes, (ii) shortage of systematic experimental data of outdoor water evaporation, and (iii) the lack of new applications. Based on the above analysis, we find that there is still much creative work to be done in this field.

In this work, we develop a novel nonstoichiometric CoWO$_{4-x}$ NP-deposited NF membrane (termed as CoWO$_{4-x}$@NF) by using a simple pouring method and evaluate its potential as a photothermal membrane for efficient solar-driven water evaporation and eutrophic lake water purification (Figure 1). The CoWO$_{4-x}$ NPs, with their ecofriendly, low-cytotoxicity, and outstanding light-stability properties, possess high optical absorbance in the whole spectral region between 450 and 2500 nm that remarkably matches the spectrum of sunlight. NF with a 3D porous structure ensures the rapid flow of water molecules during the water evaporation process, so it was selected as a support for the CoWO$_{4-x}$ NPs. We systematically investigate the outdoor water evaporation process of pure water, NF, and CoWO$_{4-x}$@NF and record the changes in humidity, temperature, and outdoor solar power density. As a result, CoWO$_{4-x}$@NF displays the best water evaporation performance compared with pure water and NF. Moreover, the eutrophic lake water purification using the CoWO$_{4-x}$@NF membrane is investigated in-depth through multivariate statistical analysis. CoWO$_{4-x}$@NF can effectively inhibit some harmful algae such as Cyanophyta and Euglenophyta, thereby effectively improving the dilemmas such as hypoxia and dirty smell at the bottom of the lake. Therefore, the CoWO$_{4-x}$@NF membrane has great potential for highly effective water evaporation and eutrophic lake water purification.

## EXPERIMENTAL SECTION

### Materials.
All the reagents were used without further purification unless otherwise indicated. Sodium tungstate (Na$_2$WO$_4$·2H$_2$O), cobalt chloride (CoCl$_2$·6H$_2$O) octyl trimethoxysilane (ODS), and ethanol were purchased from Aladdin. The nickel foam was obtained from Kunshan GuangJiaYuan New Materials Co., Ltd.

### Synthesis of CoWO$_{4-x}$ NPs.
First, the CoWO$_4$ NPs were prepared using a hydrothermal method. Briefly, 0.66 g of Na$_2$WO$_4$·2H$_2$O or 0.178 g of CoCl$_2$·6H$_2$O was dispersed in 25 mL of deionized water under magnetic stirring for 0.5 h to obtain a colorless or a pink solution. Then, the obtained pink solution was added dropwise to the sodium tungstate solution to form a purple solution. After magnetic stirring for another 30 min, the uniform purple solution was transferred to a Teflon-lined autoclave with a 100 mL internal volume. The autoclave was then heated at 160 °C for 24 h. The obtained blue products were collected by centrifugation, further washed with water and ethanol, and finally dried at room temperature for future use. The dark-blue CoWO$_{4-x}$ powders were
obtained by calcining at 550 °C for 2 h under a hydrogen/argon atmosphere.

Preparation and Hydrophobic Treatment of the CoWO4−x@NF Membrane. The CoWO4−x@NF membrane was prepared via a pouring method. Typically, 0.2 g of CoWO4−x NPs was dissolved in 5 mL of ethanol, followed by ultrasound for 10 min. The obtained dispersed solution was poured onto a nickel foam with a diameter of 3 cm and maintained for 24 h until ethanol was volatilized entirely. After that, 5 mL of toluene and 50 μL of ODS were mixed and then added to a Petri dish with a CoWO4−x@NF membrane. After 4 h in a ventilation cabinet, the hydrophobically treated CoWO4−x@NF membrane was obtained.

Characterization. The phase composition of the sample was determined by X-ray diffraction (XRD, Bruker AXS D8 ADVANCE) analysis. Transmission electron microscopy (TEM) images were obtained on an FEI Tecnai G2 F20 microscope at an acceleration voltage of 200 kV. The chemical valence of W ions was measured by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). Water contact angles (CAs) were obtained on a commercial CA system (JY-82B). Temperature changes and thermal distribution images were recorded by using an infrared (IR) camera (FLIR-E6). The water evaporation measurement was carried out using a 300 W Xe lamp (HSX-F300).

Indoor Water Evaporation Performance Tests. A CoWO4−x@NF membrane with a diameter of 3 cm was floated in a beaker containing 25 mL of water, and the beaker was placed on an analytical balance to measure the weight of evaporated water (WT30002). A Xe lamp with a power density of 1 kW m−2 (1 sun) was shined onto the membrane vertically from the top. The mass loss was recorded every 5 min, and the surface temperature of the membrane was recorded using an IR camera. The emissivities of the NF membrane, the CoWO4−x@NF membrane, and water were determined using an emissivity measuring instrument (IR-2), and their values were 0.47, 0.83, and 0.95, respectively. The IR camera used has the function of emissivity calibration (FLIR E6), and all the obtained results were calibrated before testing. The indoor temperature and humidity of the indoor water evaporation experiment were 28 ± 0.5 °C and 50 ± 5%, respectively.

Outdoor Water Evaporation Performance Test. In this experiment, we designed a device for outdoor water evaporation experiments. A CoWO4−x@NF membrane with a diameter of 18 cm was floated in a container containing 2 L of water, and the container was placed in our designed device. The water vapor condensed on the tilted quartz glass on top of the device, and then, the condensed water flowed along with the quartz glass to the inclined groove and finally to the collection bottle. The condensed water was collected with a syringe every 1 h and weighed on a balance. The power density and humidity were recorded using a power density meter and hygrometer every 1 h, respectively.

Purification Experiment of Lake Water Driven by Outdoor Water Evaporation. The device and methods used in the lake water purification experiment are the same as those used in the outdoor water evaporation test, except that the purified water is replaced by Mengxi Lake water. Mengxi Lake is located on the campus of Harbin Normal University in Harbin, Northeast China. This region has a temperate monsoon climate with long and cold winters. The ecological state of Mengxi Lake has closely affected the biodiversity in Harbin City. In recent years, the water quality of Mengxi Lake was mesotrophic to eutrophic because of the anthropogenic activity.

Phytoplankton Quantify Analysis. Water samples used for phytoplankton quantify analysis were collected from the surface of the water (depth 0−0.5 m) using a 1 L water sample bottle.
sampler and then preserved in 4% formaldehyde solution. Water samples were counted using a Zeiss microscope at 400X. Phytoplanktons were identified by genus or species, and at least 500 phytoplankton individuals were counted per sample. Phytoplankton identification was based on John et al. (John D, Whitton B, and Brook A; The New British Freshwater Algal Flora) and Krammer (Lange-Bertalot, H, Krammer, and K. Diatoms of Europe).

Multivariate Statistical Analysis. Prior analysis, the cell density matrixes of the phytoplankton were log(x+1) transformed to downweight high-cell-density species, and their normality was improved. The stabilized phytoplankton matrixes were clustered by hierarchical cluster analysis (HCA, maximum linkage method) to classify the phytoplankton communities into groups using Euclidean distance. Furthermore, principal component analysis (PCA) was used to define the treatment tolerance of phytoplanktons. Statistical analyses were performed using HemI 1.0.0.3 and Canoco for windows 4.5 software.

RESULTS AND DISCUSSION

First, the CoWO₄ NPs were synthesized via a typical hydrothermal method. The morphology of the CoWO₄ NPs was examined using TEM, and a sheet structure and a particle size of ∼50 nm can be observed (Figures 2a and S1a). As shown in the high-resolution TEM (HRTEM) image, the lattice parameter of CoWO₄ is observed to be 0.288 nm, which is attributed to the (1 1 1) plane of the monoclinic crystal of CoWO₄ (Figure S2). The low valence of W⁵⁺ was introduced into the CoWO₄ crystals by a hydrogen reduction method to adjust their absorption properties. As can be seen in Figures 2b and S1b, the morphology and size of the CoWO₄ NPs do not change significantly compared to those of CoWO₄ NPs. XRD was employed to explore the crystal phase and purity of the CoWO₄ and CoWO₄₋ₓ NPs. Figure 2c shows that all the diffraction peaks of CoWO₄ or CoWO₄₋ₓ NPs were consistent with the standard data of monoclinic-phase CoWO₄ (PDF card no. 15-0867).

The XPS analysis further demonstrated the change in the valence of the W element in samples before and after reduction. For the CoWO₄ NPs, two peaks at 37.3 eV (W 4f⁵/₂) and 35.2 eV (W 4f⁷/₂) are attributed to the spin–orbital coupling of W⁶⁺ ions (Figure 2d). Also, for CoWO₄₋ₓ NPs, except for two peaks of the W⁶⁺ ion at the same location, there are two lower-binding-energy peaks at 36.5 and 34.4 eV, which could be assigned to the W 4f⁵/₂ and W 4f⁷/₂ core levels from W⁵⁺, respectively (Figure 2e). Nanomaterials with wide absorption bands can broadly match the solar spectrum, thereby improving their water evaporation efficiency. As shown in Figure 2f, the CoWO₄ powders have strong absorption in the ultraviolet (UV) and visible regions because of their band gap of about 2.8 eV. Compared with CoWO₄ NPs, the absorption band of the CoWO₄₋ₓ powder further extends to the near-infrared (NIR) region because of the presence of W⁵⁺ on the surface and the oxygen holes produced by hydrogen reduction. These results indicated that CoWO₄₋ₓ had a better solar energy harvesting efficiency than CoWO₄ as a light absorber. As can be seen from Figure S3, the cell viability of L02 cells treated with CoWO₄₋ₓ NPs at different concentrations (15.62–1000 μg mL⁻¹) is above 80%, indicating that CoWO₄₋ₓ NPs possess a low cytotoxic effect.
Meanwhile, we also investigated the durability of the CoWO₄₋ₓ@NF membrane used for interfacial water evaporation not only in the course of water evaporation and (d) corresponding evaporation rate for water with different treatments. (e) Solar vapor-generation cycle performance of the CoWO₄₋ₓ@NF membrane.

Figure 3a-c shows scanning electron microscopy (SEM) images of NF at different magnifications. From the images, we can observe that NF has a three-dimensional porous structure, and its thickness is about 300 μm (Figure S5a–c). CoWO₄₋ₓ was deposited onto the NF surface using a pouring method because it was simpler and more efficient compared to other methods such as freeze-drying, vacuum filtration, molten salt, and electrospinning, thus making it an unparalleled advantage in actual large-scale production.33–35 From the SEM images of CoWO₄₋ₓ@NF at different magnifications, we can observe that its pore diameter (~240 μm, Figure S4b) is slightly reduced after CoWO₄₋ₓ deposition and the 3D skeleton of NF is well retained (Figure 3d–f). In comparison, CoWO₄₋ₓ@NF has a relatively smooth surface, and there are some cracks on the surface because of the evaporation of ethanol. However, interestingly enough, we did not find any falling material during the whole experiments, and the durability of the CoWO₄₋ₓ@NF membrane will be investigated in the following tests.

After CoWO₄₋ₓ deposition, the thickness of CoWO₄₋ₓ@NF increases slightly (Figure S5d–f). The SEM mapping can further prove that the CoWO₄₋ₓ NPs were successfully deposited on the surface of NF (Figure S6). The optical properties of the CoWO₄₋ₓ@NF membrane in the range of 200–2500 nm were measured with a UV–visible–NIR (UV–vis–NIR) spectrophotometer equipped with an integrating sphere (Figure 3g). Although the absorption curve of CoWO₄₋ₓ@NF is slightly different from that of CoWO₄₋ₓ powder, it still highly matches the solar spectrum and has a low reflection and transmittance in the whole range of 200–2500 nm. The hydrophobic treatment of the photothermal membrane used for interfacial water evaporation not only helps it float on the water surface but also prevents the mass loss of hydrophilic photothermal absorbers. As shown in Figure 3h, the water CAs of pure NF and CoWO₄₋ₓ@NF are 123 and 0°, respectively. After the hydrophobic treatment with ODS, CoWO₄₋ₓ@NF possesses the superhydrophobic properties (CA = 154°), suggesting that the hydrophobic treatment was successful.

To evaluate the efficient solar steam generation of pure water, NF, and CoWO₄₋ₓ@NF, water evaporation rates were cautiously measured to characterize their performance quantitatively. The surface temperature changes during simulated solar irradiation (1 sun) for different groups were recorded utilizing an IR camera. As can be seen in Figure 4a, the temperature changes (ΔT) of pure water and the NF membrane after 60 min of irradiation are 17.7 and 10.0 °C, respectively. By contrast, the surface temperature change of CoWO₄₋ₓ@NF is 20.1 °C, revealing that the deposition of CoWO₄₋ₓ NPs can improve the photothermal conversion efficiency of the NF membrane. The obtained results of time-dependent water evaporation under simulated solar irradiation are shown in Figure 4c. Pure water, NF, or CoWO₄₋ₓ@NF exhibits negligible water evaporation in 60 min without irradiation. In comparison, under simulated solar irradiation, the water evaporation of pure water at 60 min was 0.58 kg m⁻², while the water evaporation of CoWO₄₋ₓ@NF was 1.05 kg m⁻², which was 1.8 times that of pure water and 1.2 times that of NF, suggesting its excellent water evaporation performance.

As can be seen in Figure 4d, the evaporation rate of CoWO₄₋ₓ@NF at 60 min is 1.05 kg m⁻² h⁻¹, which is much higher than those of pure water (0.58 kg m⁻² h⁻¹) and NF (0.87 kg m⁻² h⁻¹). The light-to-heat conversion efficiency (η) of water evaporation can be calculated by the following equation.37

$$\eta = \frac{\text{water evaporation rate}}{\text{irradiation intensity}} \times \text{wavelength} \times \text{absorption coefficient}$$
Figure 5. (a) Photograph of outdoor water evaporation devices of different experimental groups. (b) Temperature variation from 8:00 a.m. to 5:00 p.m. in a day. (c) Power density changes from 8:00 a.m. to 5:00 p.m. in a day. (d) Humidity changes from 8:00 a.m. to 5:00 p.m. in a day. (e) Time course of water evaporation and (f) corresponding evaporation rate for water with different treatments.

\[ \eta = \frac{dm}{d\times S} \times \frac{H_e}{Q_s} \times 100\% \]

where \( m \) is the mass of evaporated water, \( t \) is the time, \( S \) is the surface area of each group, \( H_e \) is the heat of evaporation of water (~2260 kJ kg\(^{-1}\)), and \( Q_s \) is the power density of the light source (1 kW m\(^{-2}\)). Accordingly, when the light power density is 1 sun, the \( \eta \) value of CoWO\(_4\)@NF can be calculated to be 66%. Because the CoWO\(_4\)@NF membrane is in direct contact with bulk water, it will cause a large amount of heat loss during the water evaporation process. We hypothesized that the \( \eta \) value of the CoWO\(_4\)@NF membrane would be further improved by thermal insulation treatment. To verify our hypothesis, we carried out water evaporation experiments using the CoWO\(_4\)@NF membrane on a self-floating thermal insulation sponge. As can be seen in Figure S7, the results showed that the evaporation rate and the \( \eta \) value of the CoWO\(_4\)@NF membrane treated with heat insulation could be increased to 1.30 kg m\(^{-2}\) h\(^{-1}\) and 82%, respectively. The thermal conductivities were determined by the transient plane source method. The results show that the thermal conductivity of the CoWO\(_4\)@NF membrane (0.2175 W m\(^{-1}\) K\(^{-1}\)) is slightly higher than the thermal conductivity of the NF membrane (0.2111 W m\(^{-1}\) K\(^{-1}\)), but the CoWO\(_4\)@NF membrane has a higher light-to-heat conversion efficiency, so it is more suitable for water evaporation. The cycling test was carried out to demonstrate the durability of the CoWO\(_4\)@NF membrane under simulated solar irradiation. As shown in Figure 4e, after 20 cyclic tests, the highly stable relative water evaporation is achieved, revealing that the CoWO\(_4\)@NF membrane possesses excellent stability and recycling ability for solar energy-driven water steam generation applications. To verify whether the cracks on the CoWO\(_4\)@NF surface affect the mechanical properties of the CoWO\(_4\)@NF membrane, we carried out the SEM test of the membrane after 20 cycles in water. As shown in Figure S8, we can see that the corresponding water transport channels are not significantly blocked or collapsed, which can further prove that the cracks did not affect the mechanical properties of the CoWO\(_4\)@NF membrane.

As far as we know, relatively few outdoor water evaporation experiments have been reported, and most have been performed in laboratories, which is disadvantageous for potential future practical applications. At present, most scientists choose to conduct water evaporation experiments in the laboratory for the following reasons: (1) unstable water evaporation performance due to uncontrolled outdoor weather, (2) difficult preparation of large photothermal membranes due to multiple reasons, and (3) the lack of available devices for outdoor water evaporation. However, only gradually addressing the problems faced by outdoor water can promote sustainable development in this field. As can be seen in Figures 5a and S9, we used our designed water evaporation devices to evaluate the outdoor water evaporation performance of different experimental groups (from left to right are the pure water group, the NF group, and the CoWO\(_4\)@NF group). We compared the water evaporation performance of the abovementioned three groups by irradiation with natural sunlight. From Figure 5b, we can see that the temperature remains relatively stable from 8:00 a.m. to 5:00 p.m., with an average temperature of about 25 °C. Besides, we found that during the water evaporation process, the power density of the sun was minimum at 5:00 p.m. and reached the maximum at 2:00 p.m. (Figure 5c). As shown in Figure 5d, the outdoor humidity and solar power density are negatively correlated, reaching a peak at 8:00 a.m. and a minimum at 1:00 p.m. After 9 h of irradiation, the water evaporation of CoWO\(_4\)@NF was 2.91 kg m\(^{-2}\), which was 1.6 times that of pure water and 1.3 times that of NF (Figure 5e). As shown in Figure 5f, the maximum outdoor instantaneous solar evaporation rate can reach about 0.52 kg m\(^{-2}\) h\(^{-1}\), which was lower than the indoor testing result. We speculated that there might be three main
reasons: (1) the solar power density of the sunlight during the daytime did not reach 1 kW m$^{-2}$; (2) the indoor water evaporation was carried out in an open system, while the outdoor water evaporation was conducted in a closed system. With the extension of the water evaporation time, the internal humidity of the closed system reaches saturation, which prevents further evaporation of water;38 (3) in the closed system we designed, most of the water can be collected effectively. However, there is also a small amount of water which is concentrated on the glass wall and cannot be collected, which will slightly affect the calculation of the water evaporation rate.

The algae in the lake water mainly consist of Bacillariophyta and Chlorophyta. The emergence of a large amount of Cyanophyta is a sign of eutrophication of lake water, and with the development of eutrophication, the water quality finally becomes Cyanophyta-based.39,40 A massive increase in Cyanophyta and Euglenophyta can lead to deterioration of water quality and, in severe cases, the depletion of oxygen in the water, resulting in the death of fish or shrimp.41 To the best of our knowledge, the treatment of eutrophic lake water while achieving freshwater through solar-driven water evaporation has yet to be investigated. We employed Mengxi Lake water as a model of eutrophic lake water and divided the experiments into three groups, including the lake water, NF, and CoWO$_4$@NF groups. The water evaporation performance of the abovementioned three groups was analyzed by natural sunlight irradiation.

As shown in Figure 6a, the temperature in the morning is relatively low (~23 °C), and it can stabilize on average around 27 °C after midnight. As shown in Figure 6b,c, the time point at which the solar power density is maximum appears at 1:00 p.m. and the minimum value of humidity also appears at 1:00 p.m., which is consistent with the above results (Figure 5c,d). As can be seen in Figure 6d, compared with the other two groups, the CoWO$_4$@NF group still has the best water evaporation performance. Affected by the low temperature and high humidity in the morning, the water evaporation rate of
each experimental group from 9:00 a.m. to 10:00 a.m. is very slow (Figure 6e). Besides, the maximum instantaneous outdoor solar evaporation rate can reach about 0.53 kg m\(^{-2}\) h\(^{-1}\). From the above results, we can see that the as-prepared CoWO\(_4\)@NF membrane can also achieve a good evaporation effect when applied to the lake water evaporation. To evaluate the potential of the CoWO\(_4\)@NF membrane for purifying eutrophic lake water, we termed untreated water and treated water as samples 1–7 and performed statistical analysis on algae in the lake water (Figure 1). A total of 48 algae taxa, which belong to 37 genera, were identified in our study (Figure S10). PCA shows a clear difference in species composition between the different treatment samples. PC 1 clearly separates the differently treated samples from the untreated sample (Figure S11). As can be seen in Figure 6f, the phytoplankton community was mainly composed of Bacillariophyta and Chlorophyta. Compared with the cell density of sample 1 (3.7 × 10\(^4\) cell L\(^{-1}\)), the cell densities of Cyanophyta in sample 2, sample 4, and sample 6 are 4.0 × 10\(^3\), 3.5 × 10\(^3\), and 3.0 × 10\(^4\) cell L\(^{-1}\), respectively. However, the cell densities of Euglenophyta in sample 2, sample 4, and sample 6 are 5.3 × 10\(^3\), 3.5 × 10\(^3\), and 2.5 × 10\(^4\) cell L\(^{-1}\), respectively (sample 1, 6.25 × 10\(^4\) cell L\(^{-1}\)). The above results show that the CoWO\(_4\)@NF membrane with sunlight irradiation can effectively reduce the amount of Cyanophyta and Euglenophyta in lake water, which are the main factors that cause eutrophication of lake water. The inhibition rates of Cyanophyta and Euglenophyta were calculated to be 19 and 60%, respectively. The primary mechanism of the CoWO\(_4\)@NF membrane inhibiting the two algae is that the photothermal effect it produces affects the optimum temperature for the growth of the two algae.\(^{42}\) Based on previous reports, too much Bacillariophyta can also cause water quality deterioration.\(^{43}\) Compared with the cell density of sample 1 (1763.3 × 10\(^4\) cell L\(^{-1}\)), the cell density of Bacillariophyta in sample 6 is reduced by about 10 times (18 × 10\(^4\) cell L\(^{-1}\)). Interestingly, we did not find any algae in sample 3, but we found the skeleton of dead Bacillariophyta in sample S, and sample 7 (Figure S12), which is mainly due to the skeleton of Bacillariophyta with strong mechanical characteristics, could enter the collection bottle with vapor (water vapor needs to reach a certain rate).\(^{44,45}\) As depicted in Figure 6g, the taxa richness of the seven samples was in the range from 0 to 18, and none of the species was found in the entire treatment group. HCA divided the samples into two large groups: the pure lake water group (sample 1) and the treatment groups (samples 2–7). The treatment groups were further divided into two subgroups, and we can clearly find that the phytoplankton communities of sample 2, sample 4, and sample 6 were dissimilar to those of sample 3, sample S, and sample 7. From the heat map, we can observe that the water sample (sample 7) obtained after CoWO\(_4\)@NF membrane treatment mainly contains the skeletons of cymbella sp. and navicula sp., both of which belong to Bacillariophyta. Based on the above analysis, we successfully proved that the CoWO\(_4\)@NF membrane could be used for the purification of eutrophic lake water and set a model for the new application of a photothermal membrane. We further evaluated the lake water purification effect of the thermally insulated CoWO\(_4\)@NF membrane. As shown in Figure S13, compared with the pure CoWO\(_4\)@NF membrane, the lake water purification capacity of the thermally insulated CoWO\(_4\)@NF membrane is significantly reduced, indicating that the photothermal membrane mainly relies on the photothermal effect produced by itself to purify lake water. The heat insulation treatment hinders the direct contact between the membrane and the algae, thereby reducing its ability to purify lake water. In the collection of freshwater, the light-to-heat conversion efficiency of a photothermal membrane is undoubtedly important, but in the purification of eutrophic lake water, the direct contact between the membrane and the lake water is more important. Therefore, to achieve the dual purposes of collecting freshwater and purifying eutrophic lake water, we selected direct contact between the membrane and the lake water to conduct the relevant experiments. Finally, we evaluated the stability of CoWO\(_4\)@NF in the lake water. As shown in Figure S14, the CoWO\(_4\)@NF membrane still maintained relatively stable water evaporation after 20 cycles, suggesting its excellent durability in the lake water.

## CONCLUSIONS

In summary, this work has demonstrated a novel and ecofriendly CoWO\(_4\)@NF photothermal membrane synthesized via a simple pouring method for highly efficient solar-driven outdoor water evaporation and eutrophic lake water purification. Because of the strong and broad absorption of CoWO\(_4\) NPs, the CoWO\(_4\)@NF membrane displayed highly efficient water transportation from water to the surface of the photothermal membrane compared with the NF membrane. The water evaporation of CoWO\(_4\)@NF at 60 min is 1.05 Kg m\(^{-2}\) under the irradiation of simulated sunlight (1 sun), which is 1.8 times that of pure water and 1.2 times that of NF. Simultaneously, the hydrophobicity endowed the CoWO\(_4\)@NF membrane a reliable self-floating ability, while the good surface mechanical properties of the membrane made it have good durability even after 20 cycles. Notably, through the phytoplankton quantify and multivariate statistical analyses, we found that the CoWO\(_4\)@NF membrane can effectively reduce the cell density of Cyanophyta, Euglenophyta, and Bacillariophyta, which were the leading causes of deterioration of water quality, the depletion of oxygen in the water, or the death of fish. Our work has provided not only many reliable primary data for outdoor water evaporation and eutrophic water purification but also a good case for new applications of water evaporation.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03887.

Large-scale TEM images, HRTEM image, relative L02 cell viability, aperture distribution of different membranes, cross-sectional SEM images, SEM mapping, time course of water evaporation, SEM images of the CoWO\(_4\)@NF membrane after 20 cycles, designed outdoor water evaporation device, micrographs, PCA, and typical Bacillariophyta (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

Wei Guo — Key Laboratory of Photochemical Biomaterials and Energy Storage Materials, Heilongjiang Province and College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, China; orcid.org/0000-0001-5445-7872; Email: guoweii@hrbnu.edu.cn
Xinxin Lu — College of Life Science and Technology, Harbin Normal University, Harbin, Heilongjiang Province 150025, China; Email: luxinxinchina@163.com

Fengyu Qu — Key Laboratory of Photochemical Biomaterials and Energy Storage Materials, Heilongjiang Province and College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, China; Email: qufengyu@hrbnu.edu.cn

Authors

Haixia Liu — Key Laboratory of Photochemical Biomaterials and Energy Storage Materials, Heilongjiang Province and College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, China

Chunyu Yang — School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150025, China

Feng Zhang — Key Laboratory of Photochemical Biomaterials and Energy Storage Materials, Heilongjiang Province and College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, China

Huiiming Lin — Key Laboratory of Photochemical Biomaterials and Energy Storage Materials, Heilongjiang Province and College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, China

Le Zhao — Key Laboratory of Photochemical Biomaterials and Energy Storage Materials, Heilongjiang Province and College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, China

Tianyue Ma — Key Laboratory of Photochemical Biomaterials and Energy Storage Materials, Heilongjiang Province and College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03887

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (nos. 21471041, the Natural Science Foundation of Heilongjiang Province of China (nos. YQ2020B004 and JJ2020TD0027), and the Excellent Scientific Research Team Project of Harbin Normal University (no. KYXT202001).

REFERENCES

(1) Ma, T.; Yang, C.; Guo, W.; Lin, H.; Zhang, F.; Liu, H.; Zhao, L.; Zhang, Y.; Wang, Y.; Cui, Y.; Zhao, J.; Qu, F. Flexible Pt,Ni–S-Deposited Teflon Membrane with High Surface Mechanical Properties for Efficient Solar-Driven Strong Acid/Alkaline Water Evaporation. ACS Appl. Mater. Interfaces 2020, 12, 27140–27149.

(2) Liu, F.; Zhao, B.; Wu, W.; Yang, H.; Ning, Y.; Lai, Y.; Bradley, R. Low Cost, Robust, Environmentally Friendly Geopolymer-Mesoporous Carbon Composites for Efficient Solar Powered Steam Generation. Adv. Funct. Mater. 2018, 28, 1803266.

(3) Zhang, P.; Liu, F.; Liao, Q.; Yao, H.; Geng, H.; Cheng, H.; Li, C.; Qu, L. A Microstructured Graphene/Poly(N-isopropylacrylamide) Membrane for Intelligent Solar Water Evaporation. Angew. Chem. Int. Ed. 2018, 57, 16343–16347.

(4) Ye, M.; Jia, J.; Wu, Z.; Qian, C.; Chen, R.; O’Brien, P. G.; Sun, W.; Dong, Y.; Ozin, G. A. Synthesis of Black TiO2 Nanoparticles by Mg Reduction of TiO2 Nanocrystals and Their Application for Solar Water Evaporation. Adv. Energy Mater. 2017, 7, 1601811.

(5) Gao, M.; Peh, C. K.; Phan, H. T.; Zhu, L.; Ho, G. W. Solar Absorber Gel: Localized Macro-Nano Heat Channeling for Efficient Plasmonic Au Nanoflowers Photothermal Vaporization and Triboelectric Generation. Adv. Energy Mater. 2018, 8, 1800711.

(6) Mu, P.; Zhang, Z.; Bai, W.; He, J.; Sun, H.; Zhu, Z.; Liang, W.; Li, A. Superwetting Monolithic Hollow Carbon-Nanotubes Aerogels withHierarchically Nanoporous Structure for Efficient Solar Steam Generation. Adv. Energy Mater. 2019, 9, 1802158.

(7) Kiriakachichi, H. D.; Awad, F. S.; Hassan, A. A.; Bobb, J. A.; Lin, A.; El-Shall, M. S. Plasmonic Chemically Modified Cotton Nano-composite Fibers for Efficient Solar Water Desalination and Wastewater Treatment. Nanoscale 2018, 10, 18531–18539.

(8) Tao, F.; Zhang, Y.; Yin, K.; Cao, S.; Chang, X.; Lei, Y.; Wang, D. S.; Fan, R.; Dong, L.; Yin, Y.; Chen, X. Copper Sulfide-Based Plasmonic Photothermal Membrane for High-Efficiency Solar Vapor Generation. ACS Appl. Mater. Interfaces 2018, 10, 35154–35163.

(9) Zhang, C.; Yan, C.; Xue, Z.; Yu, W.; Xie, Y.; Wang, T. Shape-Controlled Synthesis of High-Quality Cu3S, Nanocrystals for Efficient Light-Induced Water Evaporation. Small 2016, 12, 5320–5328.

(10) Zhao, L.; Yang, Q.; Guo, W.; Liu, H.; Ma, T.; Qu, F. Co2.67S4Based Photothermal Membrane with High Mechanical Properties for Efficient Solar Water Evaporation and Photothermal Antibacterial Applications. ACS Appl. Mater. Interfaces 2019, 11, 20820–20827.

(11) Zhou, L.; Tan, Y.; Ji, D.; Zhu, B.; Zhang, P.; Xu, J.; Gan, Q.; Yu, Z.; Zhu, J. Self-Assembly of Highly Efficient, Broadband Plasmonic Absorbers for Solar Steam Generation. Sci. Adv. 2016, 2, e1501227.

(12) Bae, K.; Kang, G.; Cho, S. K.; Park, W.; Kim, K.; Padilla, W. J. Flexible Thin-Film Black Gold Membranes with Ultrabroadband Plasmonic Nanofocusing for Efficient Solar Vapour Generation. Nat. Commun. 2015, 6, 10103.

(13) Chen, C.; Li, Y.; Song, J.; Yang, Z.; Kuang, Y.; Hitz, E.; Jia, C.; Gong, A.; Jiang, F.; Zhu, J. Y.; Yang, B.; Xie, J.; Hu, L. Highly Flexible and Efficient Solar Steam Generation Device. Adv. Mater. 2017, 29, 1701756.

(14) Li, R.; Zhang, L.; Shi, L.; Wang, P. MXene Ti2C3: An Effective 2D Light-to-Heat Conversion Material. ACS Nano 2017, 11, 3752–3759.

(15) Wang, J.; Li, Y.; Deng, L.; Wei, N.; Weng, Y.; Dong, S.; Qi, D.; Qiu, J.; Chen, X.; Wu, T. High-Performance Photothermal Conversion of Narrow-Bandgap Ti3O5 Nanoparticles. Adv. Mater. 2017, 29, 1603730.

(16) Yao, J.; Yang, G. An Efficient Solar-Enabled 2D Layered Alloy Material Evaporator for Seawater Desalination. J. Mater. Chem. A 2018, 6, 3869–3876.

(17) Yao, J.; Zheng, Z.; Yang, G. Layered Tin Monolodendron as Advanced Photothermal Conversion Materials for Efficient Solar Energy-Driven Water Evaporation. Nanoscale 2018, 10, 2876–2886.

(18) Gao, M.; Zhu, L.; Peh, C. K.; Ho, G. W. Solar Absorber Material and System Designs for Photothermal Water Vaporization Towards Clean Water and Energy Production. Energy Environ. Sci. 2019, 12, 841–864.

(19) Zhu, L.; Gao, M.; Peh, C. K. N.; Wang, X.; Ho, G. W. Self-Contained Monolithic Carbon Sponges for Solar-Driven Interfacial Water Evaporation Distillation and Electricity Generation. Adv. Energy Mater. 2018, 8, 1702149.

(20) Zhu, L.; Gao, M.; Peh, C. K. N.; Ho, G. W. Solar-Driven Photothermal Nanostructured Materials Designs and Prerequisites for Evaporation and Catalysis Applications. Mater. Horiz. 2018, 5, 323–343.

(21) Ding, D.; Huang, W.; Song, C.; Yan, M.; Guo, C.; Liu, S. Non-Stoichiometric MoO3-x Quantum Dots as a Light-Harvesting Material for Interfacial Water Evaporation. Chem. Commun. 2017, 53, 6744–6747.

(22) Liu, H.; Yang, Q.; Guo, W.; Lin, H.; Zhang, F.; Zhao, J.; Ma, T.; Zhao, L.; Xu, N.; Wang, R.; Yu, J.; Qu, F. CoW6O19-Based...
(23) Zhao, P.; Zhang, H.; Zhou, H.; Yi, B. Nickel Foam and Carbon Felt Applications for Sodium Poly Sulfide/Bromine Redox Flow Battery Electrodes. Electrochim. Acta 2005, 51, 1091–1098.

(24) Yao, J. D.; Zheng, Z. Q.; Yang, G. W. Alloying-Assisted Phonon Engineering of Layered BiInSe6@Nickel Foam for Efficient Solar-Enabled Water Evaporation. Nanoscale 2017, 9, 16396–16403.

(25) Wu, D.; Qiu, D.; Jiang, W.; Chen, G.; An, L.; Zhuang, C.; Sun, Z. Self-Floating Nanostuctured Ni–NiO3/Ni Foam for Solar Thermal Water Evaporation. J. Mater. Chem. A 2019, 7, 8485–8490.

(26) Wang, P.; Gu, Y.; Miao, L.; Zhou, J.; Su, H.; Wei, A.; Mu, X.; Tian, Y.; Shi, J.; Cai, H. Co3O4 Nanoforest/Ni Foam as the Interface Heating Sheet for the Efficient Solar-driven Water Evaporation under One Sun. Sustain. Mater. Technol. 2019, 20, No. e00106.

(27) Shan, X.; Lin, Y.; Zhao, A.; Di, Y.; Hu, Y.; Guo, Y.; Gan, Z. Porous Reduced Graphene Oxide/Nickel Foam for Highly Efficient Solar Steam Generation. Nanotechnology 2019, 30, 425403.

(28) Chen, X.; Meng, C.; Wang, Y.; Zhao, Q.; Li, Y.; Chen, X.-M.; Yang, D.; Li, Y.; Zhou, Y. Laser-Synthesized Rutile TiO2 with Abundant Oxygen Vacancies for Enhanced Solar Water Evaporation. ACS Sustainable Chem. Eng. 2020, 8, 1095–1101.

(29) Sirirapu, V. K. V. P.; Kumar, A.; Srivastava, P.; Singh, R. N.; Sinha, A. S. K. Nanosized CoWO4 and NiWO4 as Efficient Oxygen-Evolving Electro catalysts. Electrochim. Acta 2016, 209, 75–84.

(30) Guo, W.; Guo, C.; Zheng, N.; Sun, T.; Liu, S. Cs xWO3 Nanorods Coated with Polyelectrolyte Multilayers as a Multifunctional Nanomaterial for Bimodal ImagingGuided Photothermal/Photodynamic Cancer Treatment. Adv. Mater. 2017, 29, 1604157.

(31) Wang, L.; Wang, Y.; Cheng, Y.; Liu, Z.; Guo, Q.; Ha, M. N.; Zhao, Z. Hydrogen-Treated Mesoporous WO3 as a Reducing Agent of CO2 to Fuels (CH4 and CH3OH) with Enhanced Photothermal Catalytic Performance. J. Mater. Chem. A 2016, 4, 5314–5322.

(32) Wang, Z.; Yang, C.; Lin, T.; Yin, H.; Chen, P.; Wan, D.; Xu, F.; Huang, F.; Lin, J.; Xie, X.; Jiang, M. Visible-Light Photocatalytic Solar Thermal and Photoelectrochemical Properties of Aluminium-Reduced Black Titania. Energy Environ. Sci. 2013, 6, 3007–3014.

(33) Yi, L.; Qi, D.; Shao, P.; Lei, C.; Hou, Y.; Cai, P.; Wang, G.; Chen, X.; Wen, Z. Hollow Black TiAlO3 Nanocomposites for Solar Thermal Desalination. Nanoscale 2019, 11, 9958–9968.

(34) Yang, Y.; Zhao, R.; Zhang, T.; Zhao, K.; Xiao, P.; Ma, Y.; Ajayan, P. M.; Shi, G.; Chen, Y. Graphene-Based Standalone Solar Energy Converter for Water Desalination and Purification. ACS Nano 2018, 12, 829–835.

(35) Chalà, T. F.; Wu, C.-M.; Chou, M.-H.; Guo, Z.-L. Melt Electrospun Reduced Tungsten Oxide/Polyacrylic Fiber Membranes as a Photothermal Material for Light-Driven Intercalial Water Evaporation. ACS Appl. Mater. Interfaces 2018, 10, 28955–28962.

(36) Naseem, S.; Wu, C.-M.; Chala, T. F. Photothermal-Responsive Tungsten Bronze/Recycled Cellulose Triacetate Porous Fiber Membranes for Efficient Light-Driven Intercalial Water Evaporation. Sol. Energy 2019, 194, 391–399.

(37) Zhang, L.; Tang, B.; Wu, J.; Li, R.; Wang, P. Hydrophobic Light-to-Heat Conversion Membranes with Self-Healing Ability for Interface Solar Heating. Adv. Mater. 2015, 27, 4889–4894.

(38) Guo, Y.; Zhou, X.; Zhao, P.; Bae, J.; Rosenberger, B.; Yu, G. Synergistic Energy Nanoconfinement and Water Activation in Hydrogels for Efficient Solar Water Desalination. ACS Nano 2019, 13, 7913–7919.

(39) Wang, X.; Wang, Y.; Liu, L. S.; Shu, J. M.; Zha, Y. Z.; Zhou, J. Phytoplankton and Eutrophication Degree Assessment of Baiyangdian Lake Wetland, China. Sci. World J. 2013, 2013, 436965.

(40) Xie, F.; Li, L.; Song, K.; Li, G.; Wu, F.; Giesy, J. P. Characterization of Phosphorus Forms in A Eutrophic Lake, China. Sci. Total Environ. 2019, 659, 1437–1447.

(41) Giorgi, A.; Malacalza, L. Effect of an Industrial Discharge on Water Quality and Periphyton Structure in a Pampean Stream. Environ. Monit. Assess. 2002, 75, 107–119.