An Ultrathin Flexible 2D Membrane Based on Single-Walled Nanotube–MoS$_2$ Hybrid Film for High-Performance Solar Steam Generation

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Solar steam generation is achieved by localized heating system using various floating photothermal materials. However, the steam generation efficiency is hindered by the difficulty in obtaining a photothermal material with ultrathin structure yet sufficient solar spectrum absorption capability. Herein, for the first time, an ultrathin 2D porous photothermal film based on MoS$_2$ nanosheets and single-walled nanotube (SWNT) films is prepared. The as-prepared SWNT–MoS$_2$ film exhibits an absorption of more than 82% over the whole solar spectrum range even with an ultrathin thickness of ≈120 nm. Moreover, the SWNT–MoS$_2$ film floating on the water surface can generate a sharp temperature gradient due to the localized heat confinement effect. Meanwhile, the ultrathin and porous structure effectively facilitates the fast water vapor escaping, consequently an impressively high evaporation efficiency of 91.5% is achieved. Additionally, the superior mechanical strength of the SWNT–MoS$_2$ film enables the film to be reused for at least 20 solar illumination cycles and maintains stable water productivity as well as high salt rejection performance. This rational designed hybrid architecture provides a novel strategy for constructing 2D-based nanomaterials for solar energy harvesting, chemical separation, and related technologies.

1. Introduction

A scarcity of drinking water is one of the most pervasive global crises facing humankind, and this problem has been complicated by climate change, population growth, water contamination as well as rapid urbanization.[1–3] According to statistics, the demand for freshwater is predicted to increase by more than 40% by 2050. Namely, two-thirds of the world’s population will suffer from the consequences of lack of clean water by 2025.[4] Fortunately, seawater desalination technologies, which are believed to be the only method to alleviate the problem of water shortage without impairing natural hydrological cycles, are attracting enormous research interests driven by huge ecological benefits.[1,5] Typically, the water desalination technologies include reverse osmosis,[6] capacitive deionization,[7] membrane distillation,[8–10] solar evaporation,[11] etc. In recent years, solar evaporation as a type of desalination technology has attracted considerable research attention due to its capability to harvest renewable and inexhaustible solar energy.[11–46] Currently, the researches on the solar evaporation mainly focusing on the localized heating system, which is realized by floating the photothermal materials on the evaporative surface to localize the solar energy.[11–46] This new strategy minimizes the heat losses due to the reduction of heat transfer to the non-evaporative portion in the system, thus resulting in significantly enhanced solar evaporation efficiency.[12] Recently, localized heating nanomaterials such as floating Fe$_3$O$_4$/C magnetic particles,[13] assembled plasmonic gold nanoparticles film,[42,43] and polypyrrole (PPy) coated stainless steel mesh[20] have been developed and their applications in solar evaporation have been exploited. However, the thicknesses of those materials are relatively thick to ensure the sufficient solar spectrum absorption, while the steam transport velocity would be significantly hindered by these long and tortuous pathways. Also, the inherent low chemical and mechanical stability of the developed photothermal materials need to be overcome to guarantee that the film can be recycled without influencing the structure and performance. To date, controlled synthesis of ultrathin yet high mechanical strength photothermal membrane materials with sufficient solar spectrum absorption capabilities remains a great challenge.
Carbon nanotubes (CNTs) are a typical 1D nanostructure material which possess excellent mechanical strength[47–49] and thermal transport properties.[47,50,51] As a typical CNT nanostructure, chemical vapor deposition (CVD) grown single-walled nanotube (SWNT) films are 2D porous network structures which are composed of assembled SWNT building blocks.[52–54] Owing to the ultrathin feature (less than 100 nm thickness) and hydrophobic nature, SWNT films possess outstanding permeability and breathability for water vapor. In addition, the tubular structure of the SWNT as well as the close connection between the SWNTs endues the SWNT film with high mechanical strength. Consequently, SWNT films, which exhibit full solar spectrum absorption capability, are considered as ideal candidates of ultrathin photothermal material for efficient solar steam generation. More importantly, the SWNT film with porous network structure and superior mechanical strength shows great potential to combine with other photothermal materials such as MoS$_2$,[55,56] noble metal nanoparticles,[43,57] PPY,[20] graphene,[29,31,58] or solar energy harvesting films[59–61] to obtain a hybrid solar steam generation film with synergistic photothermal properties.

Herein, for the first time, we prepared an ultrathin 2D porous photothermal membrane based on SWNT–MoS$_2$ hybrid film. The SWNT–MoS$_2$ film with a thickness of $\approx 120$ nm exhibits a spectrum absorption of more than 82%. To our best knowledge, this high spectrum absorption capability with such thin photothermal material has never been explored. Owing to the synergistic photothermal effect between SWNT film and MoS$_2$ nanosheets, the SWNT–MoS$_2$ hybrid film exhibits a high photothermal conversion efficiency in which the surface temperature of the film can easily achieve nearly 106 °C in a few seconds under 5 kW m$^{-2}$ solar light irradiation. Moreover, the ultrathin 2D porous network structure of the SWNT–MoS$_2$ film facilitates the fast steam transport and minimizes the heat loss, resulting in an impressively high evaporation efficiency of 91.5%. More importantly, the SWNT–MoS$_2$ film exhibits stable water evaporation rate and high salt rejection performance during the cycling light irradiations because of the inclusion of mechanical robust SWNT film. Our demonstration of SWNT–MoS$_2$ hybrid film represents a general strategy for constructing 2D-based nanomaterials for promising applications associated with energy conversion systems.

2. Results and Discussion

2.1. Fabrication of SWNT–MoS$_2$ Films

The schematic illustration of the fabrication of the ultrathin flexible 2D porous SWNT–MoS$_2$ film is shown in Figure 1a. First, CVD grown SWNT film is used as the substrate material. Then, a hydrothermal reaction was performed after immersing the SWNT film into the MoS$_2$ precursor solution. In this regard, amorphous MoS$_2$ homogeneously coated on the SWNT was obtained. Upon further annealing treatment, the amorphous MoS$_2$ converted to crystalized MoS$_2$ nanosheets and appears flower-like nanaassemblies anchored on individual SWNTs. The as-prepared SWNT–MoS$_2$ film can freely float on the water surface as well as convert the absorbed solar light into thermal energy to localize heat at the evaporative surface and generate water vapor, as shown in Figure 1b. Figure 1c shows the photograph of a $1.6 \times 1.3$ cm$^2$ SWNT–MoS$_2$ film which appears a dark color, indicating that the SWNT–MoS$_2$ film exhibits superior solar spectrum absorption capability. Figure 1d shows that the freestanding SWNT–MoS$_2$ film floated on the water surface can be handled with a tweezer and it was immediately contracted after lifting (Video S1, Supporting Information). Interestingly, the film quickly spread and totally expanded to its original flat structure when the film was resuspended on the water surface, demonstrating that the SWNT–MoS$_2$ film exhibits ultrathin feature and superior mechanical performance. As confirmed in Figures S1,S2, the thickness of the SWNT–MoS$_2$ film is $\approx 120$ nm. The contact angle of the SWNT–MoS$_2$ film was measured to be 86° (Figure S3, Supporting Information). The relatively hydrophilicity and excellent properties are particularly beneficial for the intimate contact between the film and water surface. More strikingly, it is found that the SWNT–MoS$_2$ film exhibits the self-floating capability. As shown in Figure 1e and Video S2 (Supporting Information), the SWNT–MoS$_2$ film can float to water surface automatically and retain the mechanical integrity even when the film was subjected to continuous and intense water waves. The self-floating capability is mainly attributed to the low density of the SWNT–MoS$_2$ film. Additionally, the intrinsic porous structure of the 2D film which enables the fast water flows across the cross-section of the film is also responsible for the self-floating capability. The prominent characteristics of ultrathin, flexible, and self-floating capability of the SWNT–MoS$_2$ film are critical for the application of the film in practical water desalination in which waves and water level changes are commonly occurred.

2.2. Structural Characterization

To unambiguously investigate the morphology and structure of the fabricated SWNT–MoS$_2$ film, we systematically performed scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterizations. As shown in Figure 2a, the low-magnification SEM image of the SWNT–MoS$_2$ film clearly reveals the 2D porous network structure, which is originated from the pristine SWNT film (Figure S4, Supporting Information). This highly interconnected porous structure as well as the microsized pores allow for easy transportation of water vapor. In addition, the presence of large amount of wrinkles in the flower-like MoS$_2$ nanosheets as well as the porous microstructures of SWNT–MoS$_2$ network enables the film with high surface roughness. As evidenced in the 3D Atomic force microscopy image shown in Figure S5 in the Supporting Information, the SWNT–MoS$_2$ film exhibits large amount of protrusions with different heights similar to the mountain ridges and valleys. This high surface roughness can effectively increase the contact area between the film and water surface, and thus leading to enlarged evaporative surface and enhanced evaporation rate. From the TEM image in Figure 2b, it can be clearly observed that the MoS$_2$ nanosheets with lateral sizes of about 18 nm are randomly connected with the adjacent nanosheets to assemble into a continuous and homogeneous MoS$_2$ layer coated on the SWNT and form a core–shell-structured SWNT–MoS$_2$
nanoassembly with the average diameter of 26 nm. It also can be seen that the pore sizes between the SWNT–MoS$_2$ nanoassemblies range from 20 to 200 nm. A representative high-resolution TEM (HRTEM) image in Figure 2c shows that the interface between the SWNT and MoS$_2$ nanosheets can be distinguished from the enclosed white areas and there is no clear interlayer gap between the two configurations, indicating that the MoS$_2$ nanosheets are closely attached on the SWNTs. It is worth mentioning that this intimate contact can facilitate the thermal transport between MoS$_2$ nanosheets and SWNTs. More importantly, the MoS$_2$ nanosheets which are composed of 5–10 layers of lamellar MoS$_2$ with interlayer spacing of 0.64 nm can be clearly observed from the HRTEM image. The selected area electron diffraction (SAED) patterns of the SWNT–MoS$_2$ film shows distinct diffraction patterns of SWNT and MoS$_2$ with different crystal planes (Figure 2d), in consistent with X-ray diffraction (XRD) patterns of the SWNT–MoS$_2$ with hexagonal phase MoS$_2$ (JCPDS number 37–1492) (Figure 2e). The original SWNT film only displays two diffraction peaks at 25.0° and 45.3° corresponding to (002) and (101) crystal planes (JCPDS number 41–1487). In comparison, the SWNT–MoS$_2$ film displays four typical diffraction peaks at 14.9°, 33.6°,
40.9°, 59.3° which can be assigned to the (002), (100), (103), and (110) crystal planes of the hexagonal phase MoS₂. Raman spectra of the SWNT and SWNT–MoS₂ films were further conducted to confirm the successful inclusion of MoS₂ in SWNT film (Figure 2f). As shown in Figure 2f, the SWNT film only shows two characteristic peaks at 1348 and 1587 cm⁻¹, corresponding to the D and G bands, respectively. The negligible D peak and high intensity ratio of \( I_G/I_D \) indicate that the SWNT film exhibits defect-free feature. Upon the growth of MoS₂, two obvious peaks arise at 381 and 405 cm⁻¹ corresponding to the \( E_{12g} \) and \( A_{1g} \) Raman modes of MoS₂ in the SWNT–MoS₂ hybrid film. Additionally, the intensities and peaks of the D and G bands of the SWNT–MoS₂ film are almost the same to the SWNT film, indicating that the introduction of MoS₂ retains the pristine structure of SWNT. The above results demonstrate that the layered MoS₂ nanostructure coating on the SWNT films were successfully obtained with the proposed method.

2.3. Optical Behaviors and Photothermal Properties

To experimentally assess the absorption capability of the designed SWNT–MoS₂ hybrid film, the spectra measurements over the whole solar spectrum range were performed. As presented in Figure 3a, in comparison to the SWNT film which shows an average solar spectrum absorption of 63%, the SWNT–MoS₂ film exhibits much improved spectrum absorption over the whole solar spectrum range from 300 to 2500 nm, demonstrating that the presence of MoS₂ nanostructures in the SWNT film leads to a distinct spectrum absorption improvement.
Moreover, the spectrum absorption capabilities of the SWNT–MoS2 films vary from 82% to 95% as the MoS2 nanosheets thickness increases from 2 to 6 nm (Figure S6, Supporting Information). It is also worth pointing out that the absorption of the SWNT–MoS2 film is comparable to enormous photothermal materials with typical thicknesses range from 2.4 µm to 15 mm (Table S1, Supporting Information). With such high absorption capability, the SWNT–MoS2 film holds great promise to enable high photothermal efficiency. In this regard, the surface temperature of the film under 5 kW m\(^{-2}\) solar irradiation was measured and the recorded data are plotted as a function of time (Figure 3b). As can be observed, the surface temperature of the SWNT film rises to a steady-state temperature of 66 °C after 2 min light irradiation. In comparison, the temperature of the SWNT–MoS2 film quickly rises to a high temperature of nearly 106 °C in a few seconds and then keeps at this steady-state temperature upon prolonging the irradiation time. The increased surface temperature of the SWNT–MoS2 film is due to the high light absorption capability as well as enhanced photothermal effect of MoS2 nanosheets. The infrared (IR) images of the film under solar irradiation for different periods were recorded simultaneously to monitor the temperature variations. Similar to the pure SWNT film, the temperature distribution across the SWNT–MoS2 film is uniform and homogeneous, demonstrating that the MoS2 nanosheets are uniformly attached on the SWNT film, which is in consistent with the SEM observations. Having confirmed the photothermal efficiency of the SWNT–MoS2 film, the thermal transport performance is also critical for the efficient evaporation. We then investigated the thermal conductivity of the SWNT–MoS2 film by the 3ω method (see Section SI-3 in the Supporting Information for details). In contrast with the steady-state techniques for the measurement of thermal conductivity which is typically inaccurate for the thin films due to the emergence of measurement errors introduced by thermal radiation and convection, the 3ω
The SWNT–MoS2 film is due to the presence of a layer of highly interconnected SWNT networks with large porosity in the hybrid film. This low thermal conductivity combined with the open network transport pathway result in a low conduction heat loss of 3.1% (see Section SI-5 in the Supporting Information for details).

The characteristics of high photothermal efficiency, localized heating effect as well as the thermal confinement capability make the SWNT–MoS2 film to serve as an ideal candidate for solar evaporation. The IR images of the SWNT–MoS2 film floated on the water surface after different periods of solar irradiation time were captured to visualize the temperature distribution of this system. As shown in Figure 3c,d, the temperature of water with and without SWNT–MoS2 film all keep an almost uniform surface temperature distribution of 25 °C before solar irradiation. Upon solar irradiation under power density of 5 kW m\(^{-2}\) for 30 s, the temperature of the SWNT–MoS2 film rapidly increased from room temperature to 33.2 °C and an obvious heat planar appears on the surface of the SWNT–MoS2 film, suggesting the efficient photo-to-thermal conversion occurs in the SWNT–MoS2 film. After prolonging the irradiation time to 10 min, the surface temperature of the SWNT–MoS2 film further increased to 44.6 °C, in contrast with the negligible temperature change (≈6 °C) of pure water. From the temperature profile versus the distance across the evaporation surface shown in Figure 3e, it can be seen that compared with the homogeneous temperature distribution of pure water, a sharp temperature gradient emerges for the water with SWNT–MoS2 film, illustrating that the efficient localized heat confinement and reduced heat loss were realized by the SWNT–MoS2 film. At the same time, the temperature variation as a function of time was recorded. As shown in Figure 3f, in comparison to pure water which exhibits a slowly temperature increase during the whole irradiation process, the evaporative surface with SWNT–MoS2 film under 5 nm MoS2 nanosheets thickness quickly rises to a high temperature of 38.5 °C after 2 min irradiation and then gradually increases to nearly 50 °C after 30 min irradiation. And for different MoS2 nanosheets thickness, the surface temperature difference from 42 to 50 °C under 2 and 6 nm coating due to the enhanced spectrum absorption ability (Figure S10, Supporting Information). In addition, the SWNT–MoS2 film shows stable photothermal performance upon exposing to recycle irradiation for six cycles (Figure S11, Supporting Information), indicating that the integration of SWNT and MoS2 not only increases the solar spectrum absorption performance, but also endows the film with high stability. Under 1 kW m\(^{-2}\) solar irradiation, the radiation and convection losses of the system were calculated to be only 2.3% and 2.7% (see Section SI-5 in the Supporting Information for details). It is noted that the striking and stable photothermal performance, extremely low heat loss as well as the superior mechanical properties are the prerequisites for efficient solar enabled evaporation.

2.4. Solar Steam Generation Experiments and Desalination Performance

To systematically quantify the solar steam generation capability of SWNT–MoS2 film, the mass change as a function of time was recorded under 5 kW m\(^{-2}\) solar irradiation (Figure 4a). It can be seen that the mass change increases linearly with increasing irradiation time. After 1 h solar irradiation, the mass changes for water with and without SWNT film were measured to be 4.2 and 1.3 kg m\(^{-2}\), respectively. In comparison, the mass change of water in the presence of SWNT–MoS2 film reaches 6.6 kg m\(^{-2}\), which are 5.1 and 1.6 times compared to that of pure water and with SWNT film. As shown in Figure 4b, the corresponding evaporation rate of water increases from 0.9 to 5.1 kg m\(^{-2}\) h\(^{-1}\) as the solar irradiation power density increases from 0.8 to 4 kW m\(^{-2}\). Especially, under solar irradiation power density of 5 kW m\(^{-2}\), the steady-state evaporation rate of water with SWNT–MoS2 film (5 nm MoS2 nanosheets thickness) reaches 6.6 kg m\(^{-2}\) h\(^{-1}\), which is higher than that of previously reported photothermal material with typical water evaporation rate of about 5.0 kg m\(^{-2}\) h\(^{-1}\) (Figure S10, Supporting Information). The reduced evaporation rate of water with SWNT–MoS2 film (MoS2 nanosheets thickness ≤4 nm) is due to the low mass loading of MoS2 and low spectrum absorption. As for the SWNT–MoS2 film with 6 nm MoS2 nanosheets thickness, the converse effect of narrowed pore size between the SWNT–MoS2 domains which reduces the vapor transport rate as well as the enhanced solar spectrum absorption results in a similar evaporation rate (6.4 kg m\(^{-2}\) h\(^{-1}\)) with that of 5 nm MoS2 nanosheets thickness. The evaporation efficiencies of water induced by the SWNT–MoS2 film under different solar irradiation power densities were also plotted. As can be seen, the evaporation efficiencies of water with the SWNT–MoS2 film all exceed 81.0% under the solar irradiation power densities from 1 to 5 kW m\(^{-2}\) and it reaches as high as 91.5% at the power density of 5 kW m\(^{-2}\). It is worth mentioning that this evaporation efficiency is higher than most of localized photothermal membranes with thicknesses larger than 2 μm (Table S1, Supporting Information). On the other hand, the evaporation efficiencies of water with and without SWNT film were calculated to be 58.9% and 17.6%, significantly lower than that with SWNT–MoS2 film. This impressive solar steam generation efficiency of the SWNT–MoS2 film is due to the ultrathin and interconnected porous structure that allows the rapid escape of the generated water vapor from the evaporative surface. What’s more, as shown in Figure 4c, the SWNT–MoS2 film shows stable evaporation rate even exposing the film under cycling light irradiation for 20 cycles. This superior reusability
is attributed to the high mechanical strength of the SWNT–MoS$_2$ film originating from the SWNT film.

To evaluate the performance of SWNT–MoS$_2$ film in real water desalination applications, the steam generation efficiency as well as the desalination capability was investigated by monitoring the mass change and conductivity of the simulated seawater (1 M KCl). As presented in Figure 4d, the presence of SWNT–MoS$_2$ film induced an enhanced evaporation rate (5.5 kg m$^{-2}$ h$^{-1}$) compared with that of pure seawater (1.1 kg m$^{-2}$ h$^{-1}$), which is consistent with the water evaporation experiment. Furthermore, the evaporation rate of seawater with SWNT–MoS$_2$ film is ≈ 83% of pure water, suggesting that the salt residues have little influence on the evaporation efficiency. Since the fabricated SWNT–MoS$_2$ film possesses ultrathin structure, the steam generation rate can be further improved by placing the system under vacuum conditions. As shown in Figure 4e, the evaporation rate of seawater in the presence of SWNT–MoS$_2$ film reaches as high as 15.6 kg m$^{-2}$ h$^{-1}$, which is nearly three times higher compared to that under atmosphere conditions (5.5 kg m$^{-2}$ h$^{-1}$), demonstrating that the vacuum condition significantly facilitates the vapor escaping across the ultrathin SWNT–MoS$_2$ film. More importantly, the
desalination performance of the SWNT–MoS2 film was evaluated by measuring the salinity of the desalinated water after different time periods of desalination. As shown in Figure 4f, the salinities of the desalinated water after different time periods all dramatically decreased to the salinity levels far below the World Health Organization (WHO) standard, suggesting that the efficient long-term and stable desalination are realized by the SWNT–MoS2 film. It is worth mentioning that the extremely low salinity of the desalinated water originates from the salt residues on the containers during the water condensation processes, which is widely observed in literature.[14,16,29,44]

3. Conclusion

To summarize, we have demonstrated the possibility and superb performance of 2D ultrathin flexible SWNT–MoS2 film as a localized photothermal membrane for highly efficient solar steam generation. Owing to the ultrathin and low density feature, the freestanding SWNT–MoS2 film shows self-floating behavior even under large water waves. The ultrathin SWNT–MoS2 film with the thickness of ∼120 nm shows an absorption of more than 82% over the full solar spectrum range. Also, the SWNT–MoS2 film exhibits excellent photothermal conversion efficiency in which the temperature at the evaporative interface reaches as high as 50 °C. Meanwhile, the low thermal conductivity of the SWNT–MoS2 film minimizes the heat loss to the bulk water and confines the heat at the evaporative surface. More importantly, the ultrathin and porous structure effectively facilitates the fast water vapor escaping, consequently an impressively high evaporation flux of 6.6 kg m⁻² h⁻¹ under atmosphere condition and evaporation rate of 15.6 kg m⁻² h⁻¹ under vacuum condition were achieved separately. In addition, owing to the superior mechanical strength, the SWNT–MoS2 film is highly stable and can be reused for multiple illumination cycles without degradation of the water evaporation and salt rejection performance. This work not only represents a novel strategy for constructing 2D-based functional nanomaterials but also provides a new avenue for the rational design of next generation solar steam generation systems.

4. Experimental Section

Preparation of CVD SWNT Film: The SWNT film was synthesized by the atmospheric pressure CVD method using the mixture solution of 1 mL xylene and ferrocene/sulfur (0.045 g/0.001 g) as precursor and catalysts, respectively. A gas mixture of Ar/H₂ (v/v = 0.85:0.15) was used as the carrier gas.[31] The CVD growth of SWNT film was carried out at 1160 °C with a carrier gas flow rate of 1500 sccm. At the beginning, the mixture solution of precursor and catalysts was injected into the upstream of the quartz tube at a rate of 1 mL h⁻¹. After 1 h growth process, the free-standing SWNT films were floating to the downstream of the quartz tube. The as-prepared SWNT films were directly peeled off from the quartz tube after cooling to room temperature. Subsequently, the SWNT films were treated by H₂O₂ and HNO₃ before deposited in the oven. After rinsing with DI water for three times, the obtained SWNT–amorphous MoS₂ films were transferred onto silicon wafers for further annealing treatment. Subsequently, the crystallized SWNT–MoS₂ films were obtained after annealing treatment under Ar atmosphere at 400 °C for 2 h.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D flexible membranes, MoS₂, solar steam generation, ultrathin membranes

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