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ORIGINAL REPORT



Gram-scale synthesis of porous three-dimensional carbon nanosheets for high efficiency clean water production

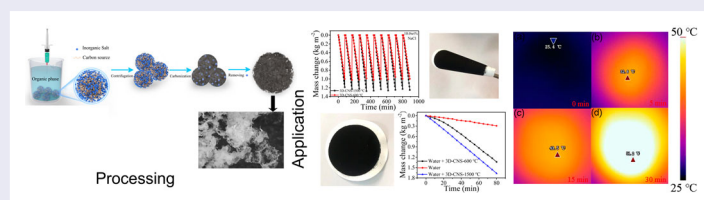
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ABSTRACT

Three-dimensional carbon nanosheets (3D-CNS) with excellent photothermal conversion (PTC) efficiency and solar evaporation performance were synthesized via a facile, versatile, and gram-scale co-precipitation carbonization strategy. Here, water-soluble biomass (protein) and inorganic salt (K_2SO_4) were co-precipitated in organic phase. The co-precipitation was then carbonized. The 3D-CNS constituted of thin, transparent, wrinkled, and interconnected nanosheets was yielded by the removal of soft template. The resulted material displayed an unprecedented PTC efficiency ($\eta = 79.76\%$) at a power density of 1.5 W cm^{-2} . The carbon-based photothermal membrane based on 3D-CNS was easily obtained by suction filtration, and exhibited excellent evaporation performance ($89.55 \pm 0.56\%$).



IMPACT STATEMENT

Three-dimensional carbon nanosheets with excellent photothermal conversion efficiency (79.76%) and solar evaporation performance (89.55%) were synthesized and demonstrated the potential application for high efficiency clean water production.

ARTICLE HISTORY

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KEYWORDS

Three-dimensional carbon nanosheets; biomass source; co-precipitation-carbonization strategy; photothermal property; solar evaporation

1. Introduction

Demand of available drinking water is soaring due to a lot of serious global problems [1–3], such as the rapid increase of population, incremental life standard, accelerated industrialization and scarcity of natural resources. Solar energy as a renewable, clean, and sustainable resource has aroused wide attention [4,5]. Reaping solar energy for production of steam is considered as one of the most energy-saving and environmental protection technologies, and has been applied to efficient seawater desalination and purification. Various photothermal materials with devisable chemistry and structures, such as polypyrrole [6,7], metal nanoparticles

[8,9], have been employed for high efficiency solar steaming. Although some reported materials show good photothermal performance [6–9], the large-scale preparation of these materials are limited due to the high production cost, such as the usage of precious metals and expensive experimental equipment. In recent years, carbon materials have attracted considerable attention due to its unique physical and chemical properties [10,11], such as high specific surface area [12], flexibility [13,14], tunable pore size, excellent photothermal conversion efficiency of near-infrared radiation (NIR) [15–18], and high evaporation efficiency for solar steaming [19]. Therefore, various carbon materials including carbon nanotubes

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[20–22], graphene [23–25], graphene oxide and carbon nanofibers [26–29] have been used in the field of solar evaporation. These carbon materials have demonstrated the potential for solar water evaporation; however, it remains a scientific challenge to prepare carbon materials with satisfactory photothermal property.

Here, we propose a facile and versatile strategy for the large-scale synthesis of three-dimensional carbon nanosheets (3D-CNS) by carbonizing co-precipitation that consisted of water-soluble biomass and inorganic salt, which we call co-precipitation carbonization strategy. 3D-CNS fabricated by the present approach possessed a 3D network, in which water steaming can move rapidly. The as-prepared 3D-CNS exhibited excellent photothermal conversion (PTC) property and a high evaporation efficiency, which is expected to employ in the fields of medical photothermal therapy for cancer, seawater desalination and purification.

2. Experimental section

2.1. The synthesis of 3D-CNS

protein (0.8 g) was dissolved in phosphoric acid buffer (20.0 mL, pH = 7.0, 0.05 mol L⁻¹) at low temperature (5°C). Then the protein solution and saturated potassium sulfate solution (60.0 mL) were mixed under stirring at low temperature until a homogeneous solution was formed. The obtained solution was dropped into ethanol (200.0 mL) by an injection pump (the rate of titration: 500 μ L min⁻¹). The precipitation was collected by centrifugation, and then carbonized by a tube furnace as the following procedure. The temperature was elevated to 350°C at a heating rate of 1°C min⁻¹ under N₂ atmosphere. After the system was maintained for 2 h, the temperature was further improved to 600°C at a heating rate of 1°C min⁻¹ and kept for 4 h. Finally, the sample was cooled down to room temperature at a rate of 5°C min⁻¹. After the obtained solid was washed with water to remove K₂SO₄ under ultrasonic condition, the 3D-CNS was obtained. Others carbon materials were prepared under the similar conditions. More details were shown in supporting information.

3. Results and discussion

3.1. Preparation scheme of 3D-CNS

Here, a facile, versatile, and gram-scalable strategy was developed for the preparation of 3D-CNS using water-soluble biomass (such as proteins, glucose, and starch) as carbon source and inorganic salt (such as K₂SO₄, NaCl and KCl) as soft template (Figure 1(a)). The solution containing water-soluble biomass is first mixed with

saturated salt solution. The uniform solution is then dropped into the water-miscible organic solvent (ethanol or isopropyl alcohol), where the salt and water-soluble biomass are co-precipitated layer by layer because they are all insoluble in organic solvent, while water is miscible with organic solvent. The obtained co-precipitation is then carbonized at different temperatures. The soft template was removed, and then the 3D-CNS was obtained.

3.2. Preparation and characterization of 3D-CNS

As a proof of concept, we dropped the solution containing protein (Bovine serum albumin) and K₂SO₄ into ethanol. The co-precipitation was collected by centrifugation. The elemental mappings display a uniform distribution of C, N, O, P, S and K element in the co-precipitation's atomic network, demonstrating K₂SO₄ and protein formed uniform co-precipitated (Figure S1). After the co-precipitation is carbonized at 600°C, the distribution of all elements has no significant change, except that the O element seems to be non-uniform distributed, which might be attributed to the dehydration during the carbonization process (Figure S2). When K₂SO₄ is removed, the resulting material (denoted as 3D-CNS-600°C) is mainly composed of C, O, N and S element, the element P and K are all invisible (Figure S3), which verify that the template has been completely removed. 3D-CNS-600°C was further treated in the range from 700 to 1500°C (denoted as 3D-CNS-700°C, 3D-CNS-800°C, 3D-CNS-900°C, 3D-CNS-1000°C, 3D-CNS-1100°C, 3D-CNS-1200°C, 3D-CNS-1300°C, 3D-CNS-1400°C and 3D-CNS-1500°C). The high re-resolution scanning electron microscope (SEM) reveals that a 3D-CNSCNS constituted of thin, transparent, ripples, wrinkled and interconnected nanosheets was achieved. The macroscopic morphologies of the materials treated at different temperatures have no significant change (Figure 1(b) (1) and (2)). Transmission electron microscope (TEM) imaging of 3D-CNS-600°C exhibits 3D interconnected structure. The edges of the 3D-CNS are composed of a stacking of carbon nanosheet with the number of layers ranging from 5–10 to 2–3 layers with the treatment temperature from 600 to 1500°C (Figure 1(b) (3–12), blue circle). Electron diffraction of the selected area (yellow circle) yield a ring-shaped pattern (inset picture in Figure 1(b)). It seems that some ripples gathered, forming scattering centers as indicated by a white circle. As the temperature of thermal reduction increases, the electron diffraction become stronger. In addition, the resulted materials were also characterized by Raman spectrum, X-ray diffraction, Fourier transform infrared, spectrum, X-ray

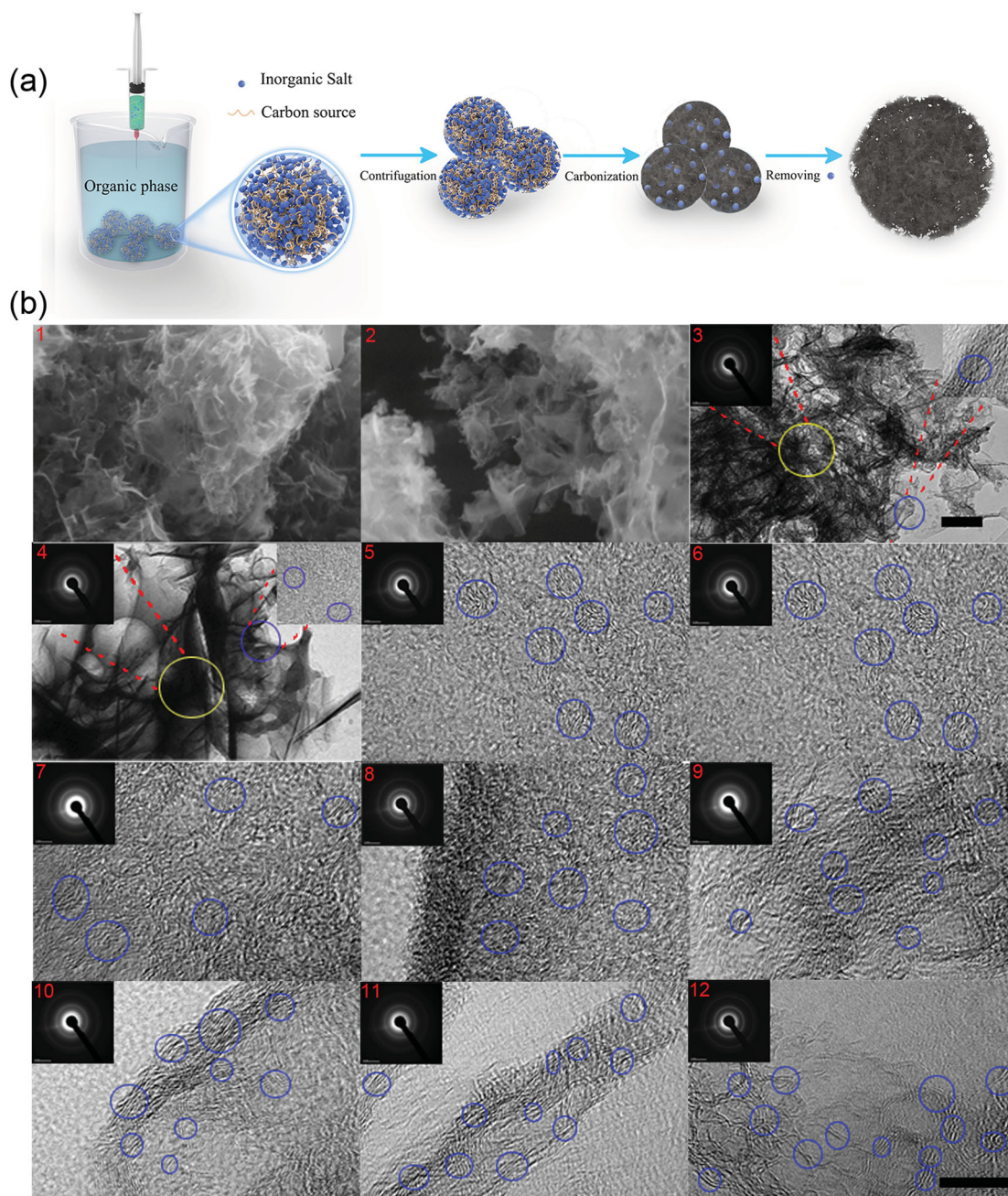


Figure 1. (a) Schematic illustrates the preparation process of 3D-CNS. (b) SEM (1, 2) and TEM (3–12) of the resulted 3D-CNS. (1) 3D-CNS-600°C. (2) 3D-CNS-1500°C. (3) 3D-CNS-600°C. (4) 3D-CNS-700°C. (5) 3D-CNS-800°C. (6) 3D-CNS-900°C. (7) 3D-CNS-1000°C. (8) 3D-CNS-1100°C. (9) 3D-CNS-1200°C. (10) 3D-CNS-1300°C. (11) 3D-CNS-1400°C. (12) 3D-CNS-1500°C. Scale bar: (3–12), 10 nm.

photoelectron spectroscopy and N_2 adsorption-desorption (Seeing Figures S4–S10 and Tables S1–S3). The results indicate that the graphitization degree, surface area, and pore size can be adjusted by the treatment temperature. The generality and practicability of the present preparation approach have also been verified by using different biomass, soft template, and solvent (Seeing Figures S11–S16).

3.3. The application of near-infrared photothermal conversion

Carbon materials have demonstrated excellent near-infrared photothermal conversion property in previous report [16,30–33]. Here, the near-infrared photothermal properties of the resulted materials were evaluated by irradiating with 808 nm laser at a power density of

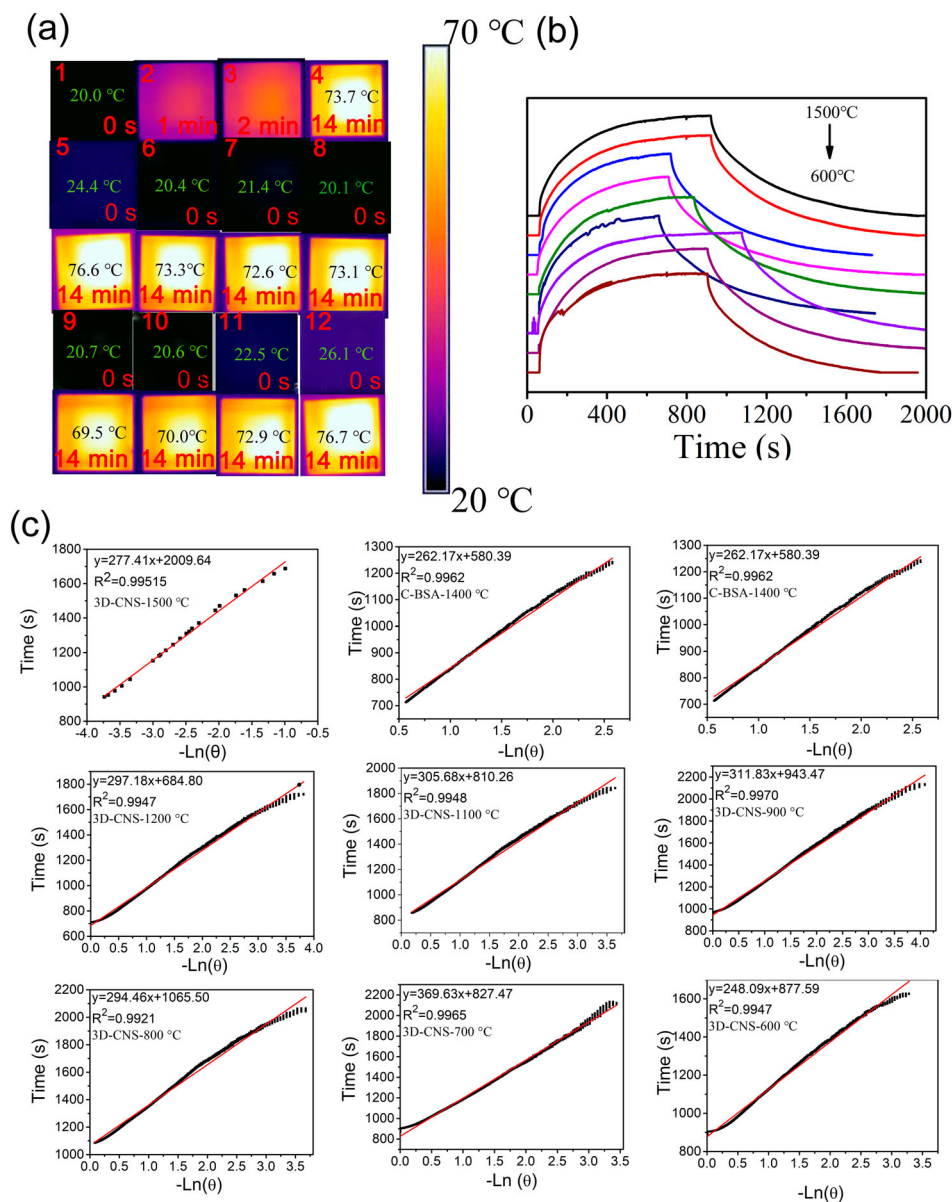


Figure 2. (a) The IR thermal images of 3D-CNS (a1-a4 corresponding to 3D-CNS-1500 °C different irradiation time, a5-a12 corresponding to 3D-CNS (600, 700, 800, 900, 1100, 1200, 1300 and 1400 °C) irradiation 14 min) with the 808 nm NIR laser (a power density of 1.5 W cm^{-2}); (b) The heating curve of the resulted materials in water under a 808 nm NIR laser at a power density of 1.5 W cm^{-2} . (c) The linear cooling time data versus $-\ln(\theta)$ obtained from the cooling period.

1.5 W cm^{-2} . The IR images were recorded simultaneously to monitor the temperature change of aqueous dispersion (Figure 2(a)). After one minute, the temperature of the solution (0.5 mg mL^{-1}) rapidly increased from 20°C to 52°C ($T_{\text{avg}} = 45^\circ\text{C}$), while the difference of temperature (DT , $DT_{\text{max}} = T_{\text{max}} - T_{\text{surr}}$) of 1.0 mL blank water sample is only 0.5°C (Figure S17). The DT increased in the order from 3D-CNS-600 to 3D-CNS-1500 °C. The PTC efficiency of 3D-CNS-1500 °C is 79.76% (Figure 2(b,c)), which is far superior to that of the recent reports [34–36]. In addition, the resulted materials prepared at different temperatures

also showed prominent photothermal property with the DT s in the range of $49.6 \sim 53.6^\circ\text{C}$ (Figure 2(b) and Table S4) and the PTC efficiency in the range of $39.53 \sim 79.76\%$ (Figure 2(c) and Table S4). The difference of the different materials might be attributed to the different solubility and crystallinity. Outstanding PTC efficiency of 3D-CNS-1500 °C might be attributed to obvious absorbance over the $250\text{--}2500 \text{ nm}$ (Figure S17b). Therefore, 3D-CNS obtained by our approach possessed great application prospects in the field of NIR photothermal conversion, seawater desalination and purification.

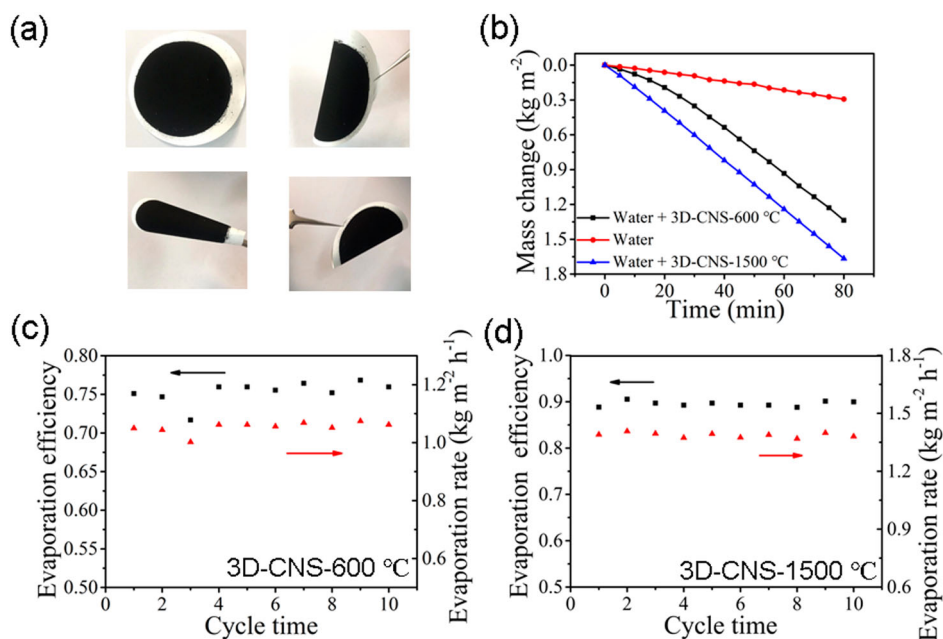


Figure 3. (a) The photograph of 3D-CNS membrane. (b) Time course of water evaporation performance under one sun solar irradiation (1.0 kW m^{-2}). (c) Cycle performance of the 3D-CNS-600°C. (d) Cycle performance of the 3D-CNS-1500°C.

3.4. The application of solar energy conversion

The solar steam generation capability of our designed 3D-CNS membrane floating on the water surface was investigated under one solar illumination power density (1 kW h^{-1}). From Figure 3(a), we can observe that the 3D-CNS membrane displays good flexibility. The mass change of water increased linearly with irradiation time at one solar illumination density (1 kW m^{-2}) (Figure 3(b)). The mass change of water is 0.29 kg m^{-2} under solar irradiation (1 kW m^{-2}) for 80 min. The presence of 3D-CNS-600°C and 3D-CNS-1500°C membranes increase the mass change of water to 1.34 and 1.64 kg m^{-2} which are 4.6 and 5.7 times more than that of pure water, respectively. The durability of 3D-CNS-600°C and 3D-CNS-1500°C membranes were investigated by 10 repeated irradiation cycle, showing reliable photothermal stability (Figure 3(c,d)). It is also worth mentioning that the evaporation rate ($1.21 \text{ kW m}^{-2} \text{ h}^{-1}$) and evaporation efficiency ($89.55 \pm 0.56\%$) of 3D-CNS-1500°C are superior to that of 3D-CNS-600°C ($1.05 \text{ kW m}^{-2} \text{ h}^{-1}$ and $75.33 \pm 1.43\%$). The surface temperature distribution of 3D-CNS-1500°C membrane was measured before and during one solar irradiation. The primary water temperature is approximately 25°C , which is basically consistent with laboratory indoor temperature. Under one sun solar illumination, the temperature rises rapidly to the maximum temperature of 36.9°C within 15 min (Figure 4). The seamless connection between matrix film and the excellent mechanical stability of 3D-CNS-1500°C film

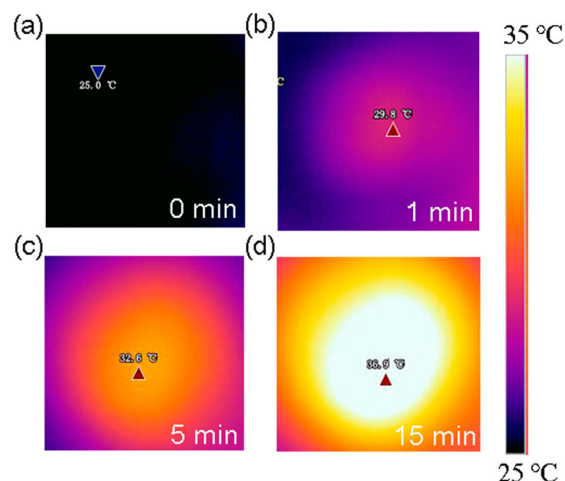


Figure 4. IR images of the temperature of vertical view for 3D-CNS-1500°C membrane under one sun solar irradiation (1.0 kW m^{-2}) at various time periods.

make water easy transport from bulk body to evaporation interface (Figure S20).

In order to further prove the practicality of our membrane, the practical desalination applications of 3D-CNS-600°C and 3D-CNS-1500°C were investigated using the representative seawater models (the Baltic Sea ($0.8 \text{ wt}\%$) and the Dead Sea ($10.0 \text{ wt}\%$)) [1]. The designed 3D-CNS-600°C and 3D-CNS-1500°C membranes show great potential to be used for water desalination. As seen in Figure 5(a), the evaporation efficiency

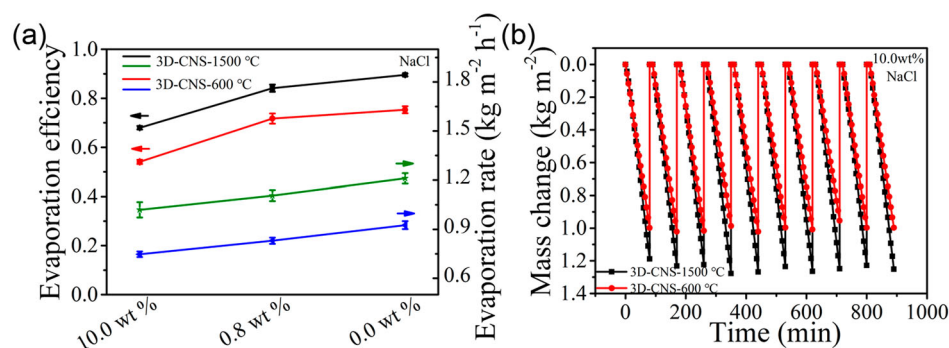


Figure 5. (a) The evaporation performance of 3D-CNS-600°C and 3D-CNS-1500°C membrane at different NaCl solution. (b) Time course of water evaporation performance of 3D-CNS-600°C and 3D-CNS-1500°C at the 10.0 wt % NaCl solution.

and evaporation rate of 3D-CNS-600°C and 3D-CNS-1500°C have no significant loss until the salinity of the simulated salt solution increases to 0.8 wt%. In addition, the durability of the 3D-CNS-600°C and 3D-CNS-1500°C membranes were investigated in 0.8 wt% (Figure S20) and 10.0 wt% NaCl by 10 repeated irradiation cycle (Figure 5(b)). The results demonstrate reliable photothermal stability.

4. Conclusions

In summary, we have developed a versatile, universal, simple, and scalable ‘co-precipitation-carbonization’ strategy for the fabrication of 3D-CNS using inorganic salt as soft template and biomass as carbon source. The resulting 3D-CNS is composed of the seamlessly interconnected carbon nanosheets, and has the unique network structure, high specific surface area, prominent PTC efficiency (79.76%) of infrared radiation and excellent solar evaporation efficiency ($89.55 \pm 0.56\%$). The resulted material is expected to apply the fields of photothermal conversion and seawater desalination and purification.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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