A 3D Photothermal Structure towards Improved Energy Efficiency in Solar Steam Generation

Yusuf Shi, Renyuan Li, Yong Jin, Sifei Zhuo, Le Shi, Jian Chang, Seunghyun Hong, Kim-Choon Ng, and Peng Wang

1Water Desalination and Reuse Center, Division of Biological and Environmental Science and Engineering, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia, 23955-6900
2KAUST Solar Center (KSC), King Abdullah University of Science and Technology, Thuwal, Saudi Arabia, 23955-6900
3Lead contact

Correspondence: peng.wang@kaust.edu.sa
SUMMARY

The energy efficiency in solar steam generation by 2D photothermal materials has approached their limit. In this work, we fabricated 3D cylindrical cup shaped structures of mixed metal oxide as solar evaporator and the 3D structure led to a high energy efficiency close to 100% under one-sun illumination due to the capability of the cup wall to recover the diffuse reflectance and thermal radiation heat loss from the 2D cup bottom. Additional heat was gained from the ambient air when the 3D structure was exposed under one sun, leading to an extremely high steam generation rate of 2.04 kg m\(^{-2}\) h\(^{-1}\). The 3D structure has a high thermal stability and shows great promises in practical applications including domestic wastewater volume reduction and seawater desalination. The results of this work inspire further research efforts to use 3D photothermal structures to break through the energy efficiency limit of 2D photothermal materials.

KEYWORDS

Solar steam generation, Photothermal materials, 3D structure, Water desalination, Wastewater treatment, Energy efficiency

INTRODUCTION

Solar steam generation, also known as solar-driven water evaporation, is emerging as a promising solar energy utilization process for clean water production.\(^1\)-\(^4\) Water evaporation process has also been utilized in wastewater treatment,\(^5\) electricity production via electrokinetic effect,\(^6\) and combined system for water desalination and electricity generation together.\(^7\) Its main advantages include that it does not need any moving parts or high pressure operations, and the solar energy is
renewable, free, clean, and widely available, which all greatly lower the operation cost. However, the relatively low power density of natural solar radiation limits the productivity of all solar-related processes. Therefore, maximizing the utilization of solar energy by all possible means is always the central topic in solar energy related applications, such as solar cell, photo(electro)catalysis, solar pond, solar drying, as well as in solar distillation, to reduce land costs and equipment capital investment.

In solar steam generation, the first strategy for maximizing the solar energy utilization is to develop photothermal materials with high light absorbance in the entire solar spectrum to capture as much sunlight as possible. The second one is to develop various heat localization techniques to diminish the heat losses, mainly focusing on cutting off the heat transfer from the top heating zone to the bulk water body without compromising water supply. Great progress has been made in these two aspects in the last five years and consequently, the energy efficiency has been pushed to the theoretical limit for two dimensional (2D) structured photothermal materials. The remaining two major energy loss pathways include the diffuse reflectance caused energy loss and the thermal radiation heat loss.

In order to further improve the energy efficiency, we designed a 3D cup shaped photothermal structure in this work. The 3D cup photothermal structure utilizes its wall to recover the energy loss caused by diffuse reflectance and thermal radiation from the 2D bottom part of the 3D cup structure, making the 3D structure no longer limited by the energy efficiency limit in 2D materials.

We first screened twenty mixed metal oxide (MMO) type inorganic pigments as light absorbing material candidates for solar steam generation by making inorganic pigment/silica composite photothermal materials using quartz glass fibrous membrane as matrix material. This MMO type material possesses high stability under strong sunlight and at high temperature in air, which makes
it fit for long-term use and it can be easily regenerated by burning in air as a solution to biofouling. CuFeMnO$_4$ with low cost, large solar absorptance and outstanding solar steam generation performance was selected from them, and it was further made into a 3D cup shaped structure as shown in (Figure 1b). Our results demonstrated that the cup wall recovers and recycles both the diffuse reflected light energy and the thermal radiation heat loss coming from the flat cup bottom, both of which lead to greatly diminished energy loss. By increasing the height of the cup wall, the 3D cup structure produces water steam with a rate of 2.04 kg m$^{-2}$ h$^{-1}$ under one-sun illumination, corresponding to an apparent energy efficiency of 140% and a net efficiency close to 100%. The supernumerary efficiency of 140% by the 3D photothermal material is attributed to its nearly full utilization of solar energy and the additional heat capture from the ambient air. The 3D design shows great promises both in seawater desalination and municipal wastewater volume reduction.

RESULTS

**Mixed metal oxide pigments screening**

Mixed metal oxide (MMO) type pigments are widely used in modern coatings as solar absorbing materials because of their excellent high temperature stability and outdoor durability. In this work, twenty Pigment/Quartz glass fibrous Composite (PQC) photothermal materials were fabricated by using quartz glass fibrous (QGF) filter membrane as matrix and corresponding metal nitrate mixture aqueous solutions as precursors (Table S1). The obtained PQC membranes are denoted as PQC-n (n = 01 - 20), and their information is listed in Table 1.

The matrix material used in this work is a commercial hydrophilic quartz glass fibrous membrane filter paper with a thickness of ~0.7 mm and an area density of 9 mg cm$^{-2}$. Water absorption experiment shows that 70 mg water can be impregnated into the pore space of 1 cm$^2$ of this QGF
membrane, indicating its porosity being approximately 94%. SEM observations (Figure S1) reveal that this QGF membrane is made of silica fibers with a wide diameter distribution range from 200 nm to more than 2000 nm.

PQC-n (n = 1 - 20) materials with 2D round shaped flat disk with diameters of 4.7 cm were first fabricated for XRD analysis, optical property investigation and solar steam generation performance evaluation (Figure 1a). Since the AB$_2$O$_4$, ABO$_3$ and ABCO$_4$ types are the major phases in MMO type pigments, we employed the metal ratio of 1:2, 1:1 and 1:1:1 in the mixed metal nitrate precursor solution. Among the MMOs, CuCr$_2$O$_4$, CoFe$_2$O$_4$, NiFe$_2$O$_4$, CuFe$_2$O$_4$, MnCo$_2$O$_4$, Co$_3$O$_4$, CoMn$_2$O$_4$, Cu$_{1.5}$Mn$_{1.5}$O$_4$, CuFeMnO$_4$ and CuCoMnO$_4$ with spinel phase structure, Mn$_2$O$_3$, FeMnO$_3$ and NiMnO$_3$ with cubic bixbyite phase structure are successfully synthesized. The others possess mixed crystal phases as listed in Table 1 and Figure S4. It should be mentioned that the crystal phase may differ from the results presented in Table 1, if the calcination temperature, calcination atmospheric composition, or other conditions are different. The PQC flat disks mostly show light colors in dry state and most of them do not show pure gray color because not all of them are black pigments (Figure S5), indicating they have undulating absorption, as shown in their UV-Vis-NIR spectra (Figure S7). This is because most of these MMO materials are narrow band gap semiconductors and their band structures greatly affect their light absorption spectra. In NIR range, some of the samples show quite high reflectance even up to 80%, which are similar to the spectra reported in literatures for MMO type pigments. Fortunately, all these samples are hydrophilic with contact angle of 0˚ (Figure S9), and they turn deep dark colors (Figure S6) with much smaller reflectance (Figure S8) once they are wetted by water. This underwater black property can be explained by the fact that their strong subsurface light scattering in dry state is significantly diminished by replacing the solid/air interface with solid/water interface.
after their pore space is filled with water in wet state. The wet sample all show relatively small reflectance in wavelength range of 1900 and 2500 nm (Figure S8) because the water inside the pore space acts as a strong NIR light absorbent in this range. The main difference in light absorbance of these wet materials is in the range between 600 and 1900 nm, which greatly affects the energy capture ability of these materials.

Solar absorptance ($\alpha$), defined as a weighted fraction between absorbed radiation energy and incoming solar radiation energy, is a more effective parameter than average absorption for solar photothermal performance evaluation since the solar spectrum is not uniformly distributed. It can be determined in terms of the surface reflectance using the following equation:

$$\alpha = \frac{\int_{2500}^{3000} I(\lambda)(1-R(\lambda))d\lambda}{\int_{300}^{2500} I(\lambda)d\lambda}$$  \hspace{1cm} (Equation 1)

where $I(\lambda)$ and $R(\lambda)$ are the light intensity function of the solar spectrum and the reflectivity function of the sample at different wavelength ($\lambda$). The transmittance is assumed to be zero, which agrees with the actual situation of our materials. $\alpha$ of all samples are thus calculated and listed in Table 1 and Figure 2 for screening. The solar absorptance values of these PQC materials in dry state are in the range of 0.510 and 0.861 and they increase to between 0.752 and 0.964 with an average increase of 0.19 in wet state (Table 1 and Figure 2). Among them, the solar absorptance of MnCo$_2$O$_4$, Co$_3$O$_4$+NiO, Co$_3$O$_4$+CuO, Cu$_{1.5}$Mn$_{1.5}$O$_4$+Mn$_2$O$_3$, Cu$_{1.5}$Mn$_{1.5}$O$_4$, CuFeMnO$_4$ and CuCoMnO$_4$ are higher than that of CuCr$_2$O$_4$ in both dry and wet states, indicating these materials possess better light capture ability than CuCr$_2$O$_4$.

The solar steam generation performance of the 2D disk shaped PQC-n membranes are evaluated by using a homemade setup under one-sun illumination as illustrated in Figure 3a. Water is transported from the bulk water to the PQC membrane by capillary effect through a pristine QGF membrane belt. This configuration leads to a slightly lower water evaporation rate but with better
accuracy, comparing to the conventional self-floating method. The results are presented in Figure S10, Table 1 and Figure 2. It clearly shows that the materials with higher solar absorptance do lead to higher evaporation rate. The spinel ferrite (CoFe$_2$O$_4$, NiFe$_2$O$_4$ and CuFe$_2$O$_4$) and cubic bixbyite phase (FeMnO$_3$ and NiMnO$_3$) materials possess significantly smaller solar absorptance and lower water evaporation rates than CuCr$_2$O$_4$ material. The pigments containing Mn, Cu and Co show generally better light absorptance than those containing Fe and Ni. Several MMO pigments, including MnCo$_2$O$_4$, Co$_3$O$_4$+NiO, Co$_3$O$_4$+CuO, Cu$_{1.5}$Mn$_{1.5}$O$_4$, CuFeMnO$_4$ and CuCoMnO$_4$, possess higher solar absorptance and better solar driven water evaporation performances than CuCr$_2$O$_4$ material. Among these metals, Cobalt ($68.0$/kg) is six times more expensive than nickel ($11.4$/kg) and ten times more expensive than copper ($6.80$/kg), while the price of Cr ($2.48$/kg in forms of Ferrochrome), Mn ($2.06$/kg), Fe ($0.069$/kg in forms of Iron Ore) are much cheaper than others (http://www.infomine.com). Among these selected pigments, Cu$_{1.5}$Mn$_{1.5}$O$_4$ and CuFeMnO$_4$ possess better performance than CuCr$_2$O$_4$, have no Cr(VI) leaching concerns, and do not contain the expensive cobalt and nickel metals, indicating they are more promising photothermal materials towards practical applications.

**3D cylindrical cup-shaped structure for steam generation and desalination**

The pristine QGF membrane is soft and fluffy and therefore it can be easily cut, bent and folded into different shapes with desired 3D structures. A cylindrical cup shaped 3D structure of PQC-19 (CuFeMnO$_4$) material was fabricated by using a cylindrical glass cup as a mold as illustrated in Figure 1b and Figure S11. The diameter of the 3D cup shaped PQC-19 material is 4.7 cm and the height of the wall is 5 cm. After loading with CuFeMnO$_4$, the composite membrane still possesses highly porous structure (Figure S2) and hydrophilic property (Figure S9). The porosity was estimated to be 92% by water absorption test. The morphology of the CuFeMnO$_4$ particles were
investigated by SEM after the silica matrix was removed by NaOH aqueous solution. It shows porous structure made of nanoparticle aggregation (Figure S3). The CuFeMnO$_4$ nanoparticles act as binder in the PQC membrane and therefore the 3D structure possesses quite good mechanical strength. It is able to hold quite a lot of water within its wall without showing any detectable shape distortion or causing any problem in operation.

The solar steam generation performance of the pristine QGF membrane, the PQC-19 materials with 2D flat disk structure and 3D cup structure were evaluated by using a setup as illustrated in Figure 3a. The water evaporation rates of pure water on the pristine QGF membrane without any pigment in dark and under simulated sunlight are measured to be 0.081 and 0.405 kg m$^{-2}$ h$^{-1}$ (Figure 3b and c) and these two values both agree with the results reported in literatures under similar conditions. The higher evaporation rate under light is attributed to the strong absorption of NIR light in the wavelength range above 900 nm, especially above 1300 nm by water. The water evaporation rate in dark does not show any distinct change when the pristine QGF membrane is replaced with 2D flat PQC-19 membrane (0.083 kg m$^{-2}$ h$^{-1}$) (Figure 3b and c) because the water/air interface area is not changed and no light absorption is involved in dark. The water evaporation rate is increased to 1.21 kg m$^{-2}$ h$^{-1}$ under light due to the excellent light absorption of the 2D PQC-19 composite membrane in wet state (Figure S8). For PQC-19 composite with the 3D cup shaped structure, its base water evaporation rate in dark is significantly increased to 0.278 kg m$^{-2}$ h$^{-1}$ due to the increased water/air interfacial area by the wall surfaces. The initial base evaporation rate is slightly higher because the evaporator and the water inside its wall are slowly cooled down due to the water evaporation, and the steady state is achieved after about 20 min. When the 3D cup structure is exposed under simulated sunlight, the steam generation rate increases to 1.73 kg m$^{-2}$ h$^{-1}$, which is 43.0% higher than that for 2D PQC-19 disk structure.
The major application for solar steam generation process is producing clean water from seawater and other water sources, especially in small scale plant and point of use apparatus. The water evaporation rate of 3.5 wt% NaCl aqueous solution and the real seawater collected from the red sea near Thuwal, Saudi Arabia were also investigated (Figure 3d). The evaporation rates under one-sun illumination for the NaCl solution (1.63 kg m\(^{-2}\) h\(^{-1}\)) and seawater (1.59 kg m\(^{-2}\) h\(^{-1}\)) are slightly smaller than that of pure water (1.73 kg m\(^{-2}\) h\(^{-1}\)) (Figure 3e), which can be ascribed to the lower water vapor pressure of the saline water. Effort is also made to build a small scale lab-made solar still to condense water vapor and collect liquid water as shown in Figure S12. When the source water is pure water, the liquid water production rates are 0.52 and 0.45 kg m\(^{-2}\) h\(^{-1}\) for 3D cup shaped and 2D flat disk shaped PQC-19 materials, respectively. When the source water is red sea seawater, the clean water production rates are slightly lowered to 0.46 and 0.39 kg m\(^{-2}\) h\(^{-1}\), respectively. In these two cases, the evaporation rates of the 3D cup structure are 16 and 18% higher than that of 2D disk structure, respectively. These results demonstrate that the 3D cup shaped structure show significantly higher solar steam generation rate than the 2D flat disk structure in the closed chamber of solar still as in open space.

In order to investigate the effect of the wall height, seven 3D cup shaped PQC-19 materials with wall height of 1, 2, 3, 4, 5, 10, and 13 cm were fabricated and their water evaporation rates in dark and under light were measured and listed in Figure 3f. The sample with 0 cm wall means the 2D flat disk sample. The water evaporation rates in dark continuously increase from 0.083, 0.103, 0.129, 0.182, 0.248, 0.278, 0.390 to 0.579 kg m\(^{-2}\) h\(^{-1}\) for the 3D cylindrical cup shaped structure PQC material with wall height of 0, 1, 2, 3, 4, 5, 10, and 13 cm, respectively, which can be ascribed to the additional water/air interface provided by the increasing cylindrical wall. When they are exposed under one-sun illumination, their evaporation rates are 1.21, 1.37, 1.43, 1.51, 1.66, 1.73,
1.84 and 2.04 kg m\(^{-2}\) h\(^{-1}\) for 3D PQC structures with wall height of 0, 1, 2, 3, 4, 5, 10, and 13 cm, respectively. If the water evaporation rate in dark is deduced from the water evaporation rate under light as in most recent literatures, the so-called net evaporation rates are 1.127, 1.268, 1.299, 1.325, 1.411, 1.452, 1.453 and 1.459 kg m\(^{-2}\) h\(^{-1}\) for 3D PQC cup with wall height of 0, 1, 2, 3, 4, 5, 10, and 13 cm, respectively. It is clear that the net evaporation rate of our 3D structures is approaching to a constant value, 1.45 - 1.46 kg m\(^{-2}\) h\(^{-1}\), when the wall height is higher than 5 cm.

**Solar steam generation for wastewater volume reduction**

Besides desalination, the solar steam generation process can also been utilized in various water removal processes, in which the collection of water steam is not necessary. One example is concentrating wastewater to reduce its volume. In this case, a 3D PQC cup with wall height of 13 cm is used as the solar evaporator to remove water from a raw wastewater collected from KAUST wastewater treatment plant. The solid content of the raw wastewater is 1.19 wt%, estimated by heating the wastewater in a blast oven at 80°C for 24 hours. The total organic carbon (TOC) value of the wastewater is 83 mg L\(^{-1}\). The setup is similar as that in Figure 3a.

55 g wastewater is loaded in a plastic container as the source water (Figure 4a). The water evaporation rate under one-sun illumination is estimated to be 1.99 kg m\(^{-2}\) h\(^{-1}\) in the first hour, which is only slightly lower than the evaporation rate measured with pure water (Figure 3f). The wastewater evaporation rate decreases to 1.74 kg m\(^{-2}\) h\(^{-1}\) after 11 hours due to the increasing concentration of the residual wastewater (Figure 4f). The wastewater evaporation rate declines quickly after 700 min when the residual waste matters turns from liquid state into solid mud state. The average water removal rate before 700 min is very impressively 1.90 kg m\(^{-2}\) h\(^{-1}\), which is greater than many state of the art 2D photothermal materials even for pure water evaporation (typically in the range of 1.20 and 1.40 kg m\(^{-2}\) h\(^{-1}\)). The residual wastewater mud is still wet with
a weight of 3.52 g, and the volume of the wastewater is decreased from 55 ml to less than 3.5 ml after this treatment, equivalent to >94% volume decrease (Figure 4b and c). The weight of the dry mud (Figure 4d) is 0.458 g, measured after the wet mud is further heated in a blast oven at 80°C for 24 hour, indicating the residual water content in the wet mud is 87 wt% and 94% of the water in raw wastewater has been removed during the solar-driven water removal process of 12 hours. In comparison, in the absence of the 3D PQC solar evaporator, the water evaporation rate of the raw water directly under one-sun illumination slowly increases to 0.70 kg m⁻² h⁻¹ after 2 hours (Figure 4f), which is actually higher than the evaporation rate of pure water under same condition because the wastewater is in brown color and therefore it possesses better light absorption ability than pure water. However, this value is still only 35% of that with 3D PQC materials. The weight of the dry mud (0.458 g) is slightly lighter than that calculated from the solid content (i.e., 0.655 g). This difference can be explained by the fact that some of the soluble solids in the raw wastewater is transferred to the PQC cup evaporator. We then measure the weight of the PQC cup and do find that its weight has increased by 0.170 g, close to the difference between the weight of the dry mud and the theoretical value. These soluble species do not affect the evaporation rate when the wet mud is replaced with the raw wastewater again as shown in Figure 4g. In each evaporation cycle, approximately 40 g wastewater is filled in the plastic bottle for treatment. In the first four cycles, the PQC cup is directly reused without any treatment and it clearly shows that the performance is almost unchanged (Figure 4g). The average evaporation rate in the first 500 min is only slightly decreased from 1.93 kg m⁻² h⁻¹ in the first cycle to 1.87, 1.87 and 1.84 kg m⁻² h⁻¹ in the second, third and fourth cycles. Before the fifth cycle, the PQC cup is washed with water and calcined in furnace in air at 600°C for 1 hour to remove possible organic foulants. After this treatment, the average evaporation rate in the fifth cycle is restored to 1.92 kg m⁻² h⁻¹ (Figure 4g).
Our results demonstrate that the PQC type photothermal material, once fouled, can be easily recovered by directly burning in air to remove all kinds of organic and bio species, and therefore they possess high potential in practical applications of solar-driven water evaporation where generally dirty source waters are involved.

DISCUSSION

Mixed metal oxide (MMO) pigments have been used in the ceramic and pottery industries for centuries and are nowadays widely used in modern coatings due to their excellent outdoor durability, chemical resistance and heat stability, which are great advantages in long-term use applications comparing to organic small molecular and polymeric pigments. Among them, those containing transition metals are mostly investigated because they possess high light absorbance due to their additional electronic transitions between their partially full “3d” orbitals. Therefore, mixed transition metal oxide with binary or trinary components were selected as candidates for screening in this work. Although several spinel chromite materials, including CuCr$_2$O$_4$ (Pigment Black 28), (Fe,Co)(Fe,Cr)$_2$O$_4$ (Pigment Black 27), (Ni, Fe)(Cr, Fe)$_2$O$_4$ (Pigment Black 30), etc. are widely used and proved to be safe for daily use, the concerns about the trace amount carcinogenic Cr(VI) leaching may affect the users’ acceptance. Therefore, in this work, we only synthesized one chromite, CuCr$_2$O$_4$, as a reference since it is the mostly used black MMO type pigment in industry and its solar-driven water evaporation performance has been carefully investigated before.

Given the nature of the feed waters, biofouling is expected to be a very serious issue in practical steam generation applications when non-concentrated sunlight is used as energy source. The temperatures of the water/air interfaces under one sun illumination are usually in the range of 30 -
45°C, which are suitable for the growth of various microorganisms. Among all light absorbing materials reported in literatures, metal oxide is the only group that can be calcined in air at 600-800°C without losing its chemical and physical integrity. This burning treatment is considered as an efficient strategy to remove bio contaminants and bio foulants for the purpose of material regeneration.

In material fabrication part of this work, we choose 700°C as the synthesis temperature and air as the atmosphere because of our intention to use burning in air at 600 - 800°C as a recovery method for photothermal materials once they are contaminated and fouled by bio- or organic contaminants. Therefore, although the MnO₂ (Pigment Black 14) and spinel phase Fe₃O₄ (Pigment Black 11) are also well-known black MMO type pigments,⁵² they do not possess enough stability in air at high temperature and it is for this reason that they are removed for further consideration in this work.

The solar absorption properties of the MMOs are mostly determined by their band structure. Most of the MMO type pigments are narrow band gap semiconductors and therefore they possess strong light absorbing capability in UV and visible light range but relatively low absorbance in NIR range as shown in Figure S7. The highest solar absorptance of these dry PQC samples is 0.86, i.e. approximately 14% solar energy will be reflected away. Since water can efficiently absorb a large portion of NIR light and decrease the subsurface light scattering, the wet PQC samples possess much higher light absorption in NIR range (Figure S8). Several samples possess excellent light absorbing capability with solar absorptance higher than 0.96 in wet state. This result suggest that the role of water in light absorbing is also very important in searching new photothermal materials.

The solar thermal water evaporation efficiency (η) is a widely used index for evaluating the performance of different photothermal materials by calculating the percentage of the energy that is utilized by water evaporation comparing to the total energy of the incident sunlight in solar
steam generation. It is generally calculated via the formula listed below as in most literature reports:

\[ \eta = \frac{\dot{m} (L_v + Q)}{P_{in}} \]  

(Equation 2)

where \( \dot{m} \) is the water mass change rate (kg m\(^{-2}\) h\(^{-1}\)), \( L_v \) is the latent heat of water evaporation (J kg\(^{-1}\)), \( Q \) is the sensible heat of water (J kg\(^{-1}\)) and \( P_{in} \) is the power of the incident simulated sunlight beam. The latent heat \( L_v \) is dependent on the temperature (\( T_i \)) of the water/air interface where the vaporization occurs. It varies from 2453 kJ kg\(^{-1}\) at 20°C to 2265 kJ kg\(^{-1}\) at 100°C (Figure S13a).\(^{55}\)

The sensible heat \( Q \) is calculated from the specific heat of water and the temperature difference between the source water (\( T_s \)) and water/air interface (\( T_i \)) (Figure S13b). The temperature of the water/air interface (\( T_i \)) greatly affects the values of both latent heat \( L_v \) and sensible heat \( Q \) and therefore affects the calculation of energy efficiency (Figure S13).

In ordered to evaluate the energy efficiency of the photothermal materials fabricated in this work, the water/air interfacial temperatures in these two cases were carefully investigated. Figures 5b and f show the IR images of the PQC-19 materials with 2D flat disk and 3D cup structures in dry states and, as seen, both of them are almost invisible, indicating they possess the same temperature and similar emissivity as the surroundings objects. When the PQC-19 materials are wetted in dark, the natural spontaneous water evaporation occurs because the humidity of the surroundings is less than 100%. The evaporation of water takes heat away and therefore decreases the temperature of the PQC cup and the water inside its pore space. The temperature of the wet 2D and 3D PQC-19 materials in dark are both approximately 16.5°C (Figure 5c and g). This temperature is about 5°C lower than the room temperature (~ 21.5°C) and it is quite close to the theoretical wet-bulb temperature under this condition.\(^{56}\) Once the temperature of the water is lower than the surroundings, it absorbs heat from the surroundings via thermal conduction, convection and
radiation. In another words, the energy driving the base water evaporation in dark is obtained from the surroundings due to the temperature difference between the wet evaporator and its surroundings. The temperature of the wet evaporator is highly dependent on the humidity and therefore greatly affects the energy flow from the surroundings to evaporator. In our experiments, the humidity was kept at ~55%. If the humidity is different, the base water evaporation rate may significantly been affected as in evaporation of open water body.\textsuperscript{57}

When the wet 2D PQC-19 disk is exposed under simulated sunlight, the steady state surface temperature is 40.5°C (Figure 5d), which is 19°C higher than the temperature of its surroundings. The latent heat and the sensible heat are calculated to be 2412 and 80 kJ kg\textsuperscript{-1} when the temperature of the water/air interface is set to 40.5°C, and therefore the energy efficiency is estimated to be 84% in this case. The major energy loss is attributed to the 4.5% diffuse reflectance and 11% thermal radiation heat loss as intensively discussed in literatures for 2D type photothermal materials.\textsuperscript{5}

In case of the wet 3D cup structure under one-sun illumination, the temperature is not uniformly distributed across the entire structure (Figure 5h). The detailed temperature distribution profiles of the bottom, inner wall and outer wall were carefully investigated (Figure S14 and S15). The flat bottom of the cup possesses the highest temperature (37-38°C) because it is directly exposed under sunlight. The temperature of the inner wall slowly decreases from ~ 37°C at the bottom part to near room temperature (RT) of 21.5°C, at the top edge part, while the temperature of the outer wall quickly drops from ~ 37°C to a temperature even lower than the RT in approximately 1 cm height (Figure S15). The majority of the outer wall is much cooler than the RT with a temperature close to 18.4°C (Figure S15).
The latent heat and the sensible heat at different parts of the PQC 3D structure are different and hard to be precisely determined since it is impossible to know how much water being evaporated in each part. While the average water/air temperature must be in the range of 19 and 38°C and therefore the theoretical limits of solar stem generation rates, calculated by setting the energy efficiency ideally as 100%, should be the range of 1.472 and 1.448 kg m\(^{-2}\) h\(^{-1}\) (Figure S13d). The net water evaporation rates for the PQC 3D cups with 5, 10 and 13 cm wall height are measured to be 1.452, 1.453 and 1.459 kg m\(^{-2}\) h\(^{-1}\) (Figure 3f) and these values are quite close to the theoretical limits (1.448-1.472 kg m\(^{-2}\) h\(^{-1}\)), indicating the energy efficiency of these 3D structures is in the range of 98.6% and 100.8%. Although it is hard to give an exact number for the energy efficiency, the energy efficiency is very close to 100% and is much higher than most reported values.

In an effort to explain the extremely efficient utilization of the solar energy by the 3D cup structure, we carefully investigate all the main energy loss pathways. The diffuse reflectance for PQC-19 materials in wet state is measured to be 4-9% in the solar spectrum range depending on the wavelength (Figure 6c), and the solar absorptance is calculated to be 0.955 (Table 1). These data is measured from the 2D flat disk sample, meaning that in case of the 2D disk, 4.5% of the solar energy is carried away by reflected lights (Figure 6a). In comparison, in the cup shaped 3D structure, most of the diffuse reflected lights from the bottom would hit on the cup wall and then be mostly absorbed by the wall (Figure 6a), which significantly reduces the energy loss caused by diffuse reflection.

In order to test and verify this hypothesis, we measured the reflectance spectra of the 3D cup structure both in dry and wet states (Figure 6c). The dry 2D disk possessed a high reflectance with a solar absorptance of 0.821, indicating 17.9% solar energy was lost via diffuse reflection. While the corresponding 3D structure possessed much lower reflectance in the entire solar spectrum
range with a solar absorptance of 0.975, indicating only 2.5% energy was lost. Since the bottom part of the 3D structure is exactly the same as the 2D disk material, this result indicates that most reflected light from the bottom 2D part is recovered by the wall of the 3D cup. In case of the wet samples, the reflectance of 3D structure is also significantly lower than the 2D disk sample, and therefore the solar absorptance of 3D structure (0.994) is much higher than that of 2D sample (0.955). The above results indicate that approximately 86% reflected light was recovered by the wall, proving the effectiveness of the cup wall in recovering the diffuse reflected light.

Thermal radiation heat loss is the main heat loss pathway in the current 2D photothermal materials, especially under one sun condition. In case of the 2D flat PQC material, the top surface temperature under light is approximately 19°C higher than RT, which leads to an approximately 11% heat loss via thermal radiation (Figure 6b). Most recently reported 2D materials possess similar energy efficiency (83 - 89%) under one sun illumination, which can be explained by that all these materials are approaching the theoretical limit of 2D material in energy efficiency, because the energy loss via reflectance (2-5%) and thermal radiation heat loss (8-12%) is occurring in all 2D materials.

For the 3D cup structure, the heat radiation from the cup bottom is towards all directions, which is quite similar with diffuse reflected lights, and similarly most of it will hit onto the much cooler wall (Figure 6b). Consequently, the radiation heat loss from the cup bottom will be mostly recovered by the wall, similar to the case of the light diffuse reflection. According to the mechanism illustrated in Figure 6a and b, the percentages of the diffuse reflectance and thermal radiation that can be recovered by the wall are mainly determined by the height to diameter ratio of the cup.

An additional energy recovery mechanism may also contribute to the high energy efficiency. In the conventional model, the source water is heated by the 2D photothermal material and converted
to hot vapor, which is 40.5˚C for 2D PQC-19 material, and then the hot vapor directly left the system. In case of the 3D cup structure, water is heated to 38˚C and converted to 38˚C vapor at the bottom part in the first stage. When the hot vapor diffuses from the bottom to upper part inside the cup, some of the heat will be transferred to the wall by conduction, convection and also heat radiation. Consequently, the hot vapor is cooled down to near room temperature before it left the system. The corresponding energy from this cooling process is reused by the wall to drive the water evaporation process at 18.4˚C on the outer wall (Figure S16). In another word, part of the absorbed solar energy is used for two times, and therefore it further increase the energy efficiency (Figure S16). In conclusion, the energy loss from the 2D bottom via light diffuse reflection, heat radiation and heating the air, can all be partially recovered and reused by the upper and cooler wall of the 3D structure, which leads to the water evaporation efficiency being nearly 100%.

One interesting phenomenon is that the temperature of the inner wall is significantly higher than that of the outer wall with 5-10˚C temperature gradient when the 3D cup structure is exposed under simulated sunlight (Figure S15), despite that the thickness of the wall is thinner than 0.7 mm. It can be explained as follows: Firstly, the inner wall gains energy by recovering the diffuse reflected light and thermal radiation from the bottom part, while the outer wall does not. Secondly, more water is evaporated on the outer wall surface than the inner wall surface because the humidity in the surroundings outside is ~55% while the humidity inside the cup is near 100%. The large temperature difference between the inner wall and the outer wall is another proof of the energy recovery mechanism.

The energy loss by reflectance and thermal radiation loss is estimated to be approximated 15.5% for 2D PQC-19 material, agree with the fact that the calculated energy efficiency of the 3D cup structure is 14-16% higher than that of 2D counterpart. While the evaporation rate of 3D PQC-19
material is 43% higher than that of 2D PQC-19 material (Figure 3c), and this is much higher than the energy efficiency difference between the 3D and 2D structures. This is because the some additional excess evaporation is coming from the additional energy gained by the outer wall from its surrounding for 3D cup structure, which is excluded in energy efficiency calculation when the base water evaporation is deduced from the evaporation rate. Since the temperature of the evaporator is greatly affected by the humidity of the surroundings, this additional excess evaporation is highly depend on the humidity of the surroundings and may almost eliminated when the humidity of the surrounding is close to 100%, such as in a sealed space like inside a solar still. And therefore, the evaporation rate of the 3D structure is only 16-18% higher than that of 2D counterpart in solar still desalination part in this work. In another hand, if the humidity is lower than 100%, which is a common condition in open space, the wall of the 3D structure will gain additional energy from the surrounding and contribute a lot to the evaporation as in our case, which is benefit for applications those do not need to collect the condensation and the water removal is the only main target, e. g. wastewater volume reduction.

**EXPERIMENTAL PROCEDURES**

**Materials.**

Quartz glass fibrous (QGF) filter membrane without binder with 20×25 cm size are purchased from Merck Millipore Ltd. (Catalogue Number AQFA8X105). Cr(NO$_3$)$_3$.9H$_2$O, Mn(NO$_3$)$_2$.4H$_2$O, Fe(NO$_3$)$_3$.9H$_2$O, Co(NO$_3$)$_2$.6H$_2$O, Ni(NO$_3$)$_2$.6H$_2$O, Cu(NO$_3$)$_2$.3H$_2$O and NaCl were purchased from Sigma-Aldrich. All aqueous solutions were prepared using deionized (DI) water with a resistivity of 18.2 MΩ cm prepared by Millipore system.

**Fabrication of PQC membranes with different structures**
QGF filter membrane paper was used as the matrix materials. It was made into cup shape as illustrated in Figure 1 by using a glass cup as mold. Metal nitrates with desired molar ratio were dissolved in water to make a clear aqueous solution with desired concentration as the precursor solution for each aimed specific pigment with \( \text{AB}_2\text{O}_4 \), \( \text{ABO}_3 \), or \( \text{ABCO}_4 \) type formula. After the pristine QGF was made into cup shape by wrapping around on the outer surface of the glass mold, the precursor aqueous solution was slowly dropped onto the membrane and the impregnation amount was 0.7 mL precursor solution per each square centimeters area of the QGF membrane in all cases. The concentration of the precursor was varied for different pigments based on theoretical calculation to ensure the loading amount of all pigment in all cases was 3 mg cm\(^{-2}\). The QGF membrane, soaked with the precursor solution, was dried along with the glass mold in a blast oven in air at 120°C for one hour. The water solvent and part of the crystal water was removed and thereafter the cylindrical cup shape of the membrane was fixed by the solidified metal nitrate mixture precursors. The composite structure with 3D cylindrical cup shape was then separated from the mold and calcined in a furnace at 700°C for 4 h with a ramp of 5°C/min. During the calcination, the shape of the 3D cup structure was well retained without noticeable distortion. The 2D flat disk samples with diameter of 4.7 cm were analogously fabricated by using flat glass plate as mold and the pigment loading amounts are fixed at 52 mg, which is equivalent to a loading amount of 3 mg cm\(^{-2}\).

**Water absorption test to determine the pore volume of the membrane**

The area of the membrane was measured by a Vernier caliper. The membrane was put on a flat glass plate horizontally and the total dry weight was measured by an electronic balance. Pure water was dropped onto the horizontally placed membrane until the membrane was clearly over soaked with water. Then the glass plate was perpendicularly placed for 1 min to drain the overloaded water
by gravity. The wet weight of the sample was measured. The difference in weight before and after wetting was regarded as the water absorption capability of the membrane and the pore space was thereafter calculated. Since the ambient temperature was ~ 21.5°C, the density of water used in the calculation was 0.998 g cm⁻³.

**Water evaporation rate measurement**

The 2D round shaped PQC flat disks or the 3D cup shape PQC materials with diameter of 4.7 cm were put on top of a square expanded polystyrene (EPS) foam with a side length of 10 cm and a thickness of 1 cm. The EPS foam was put on top of a glass bulk water cup container with diameter of 5.0 cm and height of 6 cm. Water was transported from the bulk water to the PQC membrane by capillary effect and transpiration effect via a pristine QGF belt through a hole in center of the EPS foam. The wet QGF strip is very soft and flexible and thus it can easily build a strong contact with the PQC evaporator by capillary force and provide efficient water supply. As the pristine QGF belt the PQC membrane were both wetted by water, they tightly stuck together because of the strong capillary force and thus there was an efficient connection for water transport. No extra press was needed for fixing them together. The simulated sunlight source was provided by a Newport 94043A solar simulator with an optical filter for the standard AM 1.5G spectrum. The beam size (10 × 10 cm) is slightly larger than the photothermal material and exactly perpendicular to the bottom of the cup. The weight change was monitored by an electronic scale and the real time data was collected by a computer with a sampling rate of 1 point per minute for the determination of water evaporation rate. All in-lab measurement were conducted at an ambient temperature of 21-22°C with humidity of ~55%. In this work, pure water, 3.5 wt% NaCl aqueous solution, red sea seawater and raw wastewater collected from KAUST wastewater treatment plant were used to characterize the performances of the materials.
Characterizations

The surface morphology of the membranes was investigated by field-emission scanning electron microscopy (SEM, Zeiss Merlin). The powder X-ray diffraction patterns were recorded on a Bruker D8 Discover diffractometer using Cu Kα radiation (λ=1.5418 Å) as X-ray source. The UV-Vis-NIR diffuse reflectance, transmittance and absorption spectra of the samples were recorded with an Agilent Cary 5000 spectrophotometer, with fine BaSO₄ powder as reference.

SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures and additional figures and can be found with this article online at https://doi.org/10.1016/j.joule.XXXXX.

AUTHOR CONTRIBUTIONS

Y.S. and P.W. designed the experiments. Y.S. conducted the experiments. Y.J., C.Z. and S.H. helped in solar steam generation measurement. L.S. helped in wastewater volume reduction. R.L. and K.N. drew the schematics and helped in IR images and mechanism discussion part. S.Z. did the SEM characterization. All the authors contributed to writing and revising the paper.

DECLARATION OF INTERESTS

P.W., Y.S. and C.Z. have a patent application related to the work presented in this paper.

ACKNOWLEDGMENTS

The authors are grateful to KAUST for very generous financial support.
REFERENCES


Figure Legends

Figure 1. (a) Photo images of the 2D round shape QGF membrane, the PQC-19 material (CuFeMnO$_4$) and the intermediate products. The gray PQC-19 product turns into deep dark color after wetting by water. (b) The scheme for the synthesis procedure of 3D cup shape PQC type photothermal materials.

Figure 2. The solar absorptance of PQC materials in dry (the narrow brown bar) and wet (the broad hollow blue bar) states, and their solar steam generation rates (●) under one-sun illumination.

Figure 3. (a) The scheme of the lab-made systems for solar steam generation performance measurement. (b) The water mass change curves and (c) the corresponding water evaporation rate curves for the 2D pristine QGF membrane disk without any pigment, the PQC-19 material with 2D round shaped flat disk structure and 3D cylindrical cup-shaped structure. (d) The water mass change curves and (e) the corresponding evaporation curves of different source water using 3D cup shaped PQC-19 materials as evaporator. (f) The evaporation rate recorded in dark (R$_{\text{dark}}$), under light (R$_{\text{light}}$) and their difference (R$_{\text{net}}$ = R$_{\text{light}}$ - R$_{\text{dark}}$) of the 3D cup shaped PQC-19 materials with different wall height.

Figure 4. Photo images of (a) raw wastewater, (b, c) wet mud after solar-driven water removal, (d) dry mud after oven heating in a plastic bottle. (e) The mass change curves of the wastewater under one-sun illumination with and without 3D cup shaped PQC-19 material as solar evaporator and (f) their corresponding water removal rates. (g) The reusability of the 3D cup shaped PQC-19 materials in wastewater treatment.
**Figure 5.** The images of PQC-19 materials with (a) 2D flat disk and (e) 3D cup structure in wet state, and the corresponding IR images in (b, f) dry state, (c, g) wet state in dark, and (d, h) wet state under one-sun illumination.

**Figure 6.** The schemes of energy loss pathways, (a) diffuse reflection and (b) thermal radiation, for photothermal materials with 2D disk structure and 3D cup structure. It shows the cup wall can efficiently recycle the diffuse reflection light and thermal radiation. (c) The reflectance spectra of POC-19 material with 2D disk and 3D cup structures in dry and wet states.


**Tables**

**Table 1.** The crystal phase, solar absorptance and water evaporation rates under one sun illumination of the pigment/quartz glass fibrous composite membrane samples (PQC-n, n = 1-20) with 2D disk structure.

<table>
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<tr>
<th>Samples</th>
<th>Crystal phase</th>
<th>Solar absorptance</th>
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<td>Dry</td>
<td>Wet</td>
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Figure S1. SEM images of pristine quartz glass fibrous (QGF) membrane.

Figure S2. SEM images of CuFeMnO$_4$/quartz glass composite membrane PQC-19.

Figure S3. SEM images of CuFeMnO$_4$ particles after the quartz glass was removed by NaOH aqueous solution from PQC-19 composite membrane.
Figure S4. Powder XRD patterns of the PQC products (PQC-n, n= 01-20) with different mixed metal oxide pigments. In those samples with mixed phases, the minor phase is listed after the major phase in the right column and the diffraction peaks of the minor phase is indexed by “●” in the XRD pattern, and the other diffraction peaks are belong to the major phase.
Figure S5. Optical images of the PQC materials (PQC-n, n= 01- 20) in dry states. The loading amount is fixed at 3 mg cm\(^{-2}\) for all samples.

Figure S6. Optical images of the PQC materials (PQC-n, n= 01 - 20) in wet states. The loading amount is fixed at 3 mg cm\(^{-2}\) for all samples.
Figure S7. The reflectance spectra of PQC-n (n = 01 - 20) materials in dry state. In each raw, the Y-axis starts from 0% and ends at 100%.
Figure S8. The reflectance spectra of PQC-n (n = 01 - 20) materials in wet state. In each raw, the Y-axis starts from 0% and ends at 50%.
Figure S9. The contact angle measurement of water on PQC-19 material.

Figure S10. (a) The water evaporation mass change curves of PQC-n (n = 01-20) materials with 2D flat disk structure under one-sun illumination, and (b) the corresponding water evaporation rate curves. The water evaporation rate data listed in Table 1 are calculated from the mass change curves in the range of 20 and 60 minutes.
Figure S11. The 3D cylindrical cup shaped PQC-19 material viewed from different directions.

Figure S12. The scheme of the lab-made solar still. The container is made of polypropylene (PP) plastic and the top cover is made of a polycarbonate (PC) plastic film. A aluminum foil with a round hole is covered on the PC film to ensure the sunlight can only pass through the hole to the PQC materials without heating the other parts of the solar still.
Figure S13. (a) The latent heat of water evaporation at different water/air interface temperature, which is calculated by an empirical formula: \( L_v(T_i) = 1.91846 \times 10^6\left(T_i/(T_i-33.91)\right)^2 \) according a literature.\(^{50}\) (b) The sensible heat of water at different temperature, which is calculated by the equation: \( Q = c (T_i - T_s) \), where \( c \) is specific heat of water, \( 4.2 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1} \), the \( T_i \) is the temperature of the water/air interface and \( T_s \) is the temperature of the source water, which is 21.5°C in our case. (c) The total energy input that is needed for water evaporation at different water/air interface temperature, which is calculated from latent heat plus sensible heat. (d) The theoretical water evaporation rate estimated by setting the energy efficiency to 100%. Note: The temperature of source water is set as 21.5°C for the calculation in Figure S9b, c and d.
Figure S14. Three 3D PQC-19 cylindrical cup structure with diameters of 4.7 cm and wall heights of (a) 8.5 cm, (b) 5.0 cm and (c) 2.5 cm for IR image observation. A perpendicular slit was intentionally designed in the wall of each cup structure for taking IR image of the inner wall.

Figure S15. The IR images of three 3D cup shaped PQC-19 materials with wall height of (a-d) 2.5, (f-i) 5.0 and (k-n) 8.5 cm during evaporation process (a, c, f, h, k, m) in dark and (b, d, g, i, l, n) under one-sun illumination, and (e, j, o) the corresponding temperature distribution line profiles derived from the white dash lines as marked in the IR images. The bottom of the cup is set as the zero point of the height. The IR images of inner surfaces are recorded through the slits on the wall.
Figure S16. (a) The energy consumption scheme in solar-driven water evaporation process for 2D photothermal material. (b) The energy consumption and recovery scheme in solar-driven water evaporation process for 3D cup shaped photothermal material.