

Modular Deformable Steam Electricity Cogeneration System with Photothermal, Water, and Electrochemical Tunable Multilayers

Fan Lu Meng, Minmin Gao, Tianpeng Ding, Gamze Yilmaz, Wei Li Ong, and Ghim Wei Ho*

Capturing solar energy for thermal conversion in a highly efficient manner for steam-electricity cogeneration is particularly opportune in the context of optimal solar energy utilization for concurrent water-energy harvesting. Herein, an integrative photothermal evaporator/thermogalvanic cell with the desired optical, heat, water, and electrochemical management for synergistic steam-electricity production is reported. Versatile layer by-layer assembly is employed to integrate a hydrogel/metal-oxide/polymer into a multilayer film with individually addressable thickness, composition, and structure. As such, the ultimate integrative multilayer film cell demonstrates a unified high surface area and conductive electrodes, broadband absorption, rapid water suction-ion exchange, and thermal insulation properties. Thus, the designed cell immensely suppresses heat losses, achieving a high solar thermal conversion efficiency of 91.4% and maximum power outputs of \approx 1.6 mW m⁻². Additionally, the selffloating, deformable, modular integral device presents appealing attributes such as salt-rejection for viable seawater desalination, high mechanical stability, and resilience to demanding operating conditions, and configurable on-demand/ point-of-use tandem structure to maximize clean water and power generation value per area. This integrated strategy may provide prospective opportunities to reduce dependence on fossil fuels and freshwater inputs and solutions for renewable and decentralized clean water and electricity.

1. Introduction

Harvesting solar thermal energy to heat up water can enable evaporation for seawater desalination, wastewater purification, clean water production, power generation, etc. represents

Dr. F. L. Meng, Dr. M. Gao, Dr. T. Ding, Dr. G. Yilmaz, Dr. W. L. Ong, Prof. G. W. Ho
Department of Electrical and Computer Engineering National University of Singapore
4 Engineering Drive 3, Singapore 117583, Singapore
E-mail: elehgw@nus.edu.sg
Prof. G. W. Ho
Institute of Materials Research and Engineering
A*STAR (Agency for Science, Technology and Research)
2 Fusionopolis Way, Innovis, Singapore 138634, Singapore

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.202002867.

DOI: 10.1002/adfm.202002867

one of the most promising technologies for solar energy utilization.^[1-8] Localized photothermic interfacial water evaporation confined in nanostructured solar absorbers is intensively investigated due to the significant cutback in heat losses and impressive conversion efficiency.[9-12] Prudent optimization of the optical, thermal, and water management of the solar thermal devices is the key undertakings. Specifically, maximizing the solar energy absorption in the full spectrum via screening absorber materials and choreographing design of micro- and nanostructures represents the first strategy.^[13–15] The second is to furnish thermal insulation to suppress the heat losses and create a hot concentrated region around water-air interface to accelerate evaporation.[16-20] Next is to facilitate water-holding capacity and fast ion-exchange ability between the interface and water supply to ensure continuous water delivery and prevention of salt deposition.[21] Currently, various photothermal materials and structures have been developed,^[22-32] however, their practical deployment is still restricted by

either complex synthetic procedure, poorly integrated multicomponents/dimensional features or structural configuration, as well as unsatisfactory environmental resistance (such as against highly redox chemicals, radical pH and/or hypersaline conditions) for long-term reliability.

In addition, harvesting low-grade heat loss along with water evaporation to unleash the full potential of solar thermal energy utilization is an extra incentive, which rarely earns enough attention. Thermoelectric generator particularly the thermogalvanic cell with the advantages of comparatively high Seebeck coefficient, cost-effective, and simple manufacturing process, is one attractive way to utilize the temperature gradient across the space between hot upper solar absorber and cold bulk water to convert thermal energy directly into electricity based on temperature-dependent entropy changes triggered by electron transfer between redox couples and electrodes.^[33–37] The key is to adopt and devise materials features into a harmonious photothermal evaporation and thermogalvanic energy generation system in order to maximize solar thermal benefits.



Moreover, an integrated design and operation is economical, land-saving, and effective in solving inextricably dependent energy-water nexus, which also circumvent individual systems cumulative heat losses that further undermine thermal utilization.

www.advancedsciencenews.com

Herein, we reported synergistic photothermic vaporization and thermal energy generation on an integrative evaporator/ thermogalvanic cell by optimizing the optical, heat, water, and electrochemical management. A versatile and scalable methodological platform of layer-by-layer assembly is adopted for tunable film thickness and materials constituents (hydrogel/ metal oxide/polymer) into a multilayer film with individually addressable thickness and composition to form a conformal coating on hierarchical nanostructures toward a unitary sandwiched/vertically stacked hybrid device. Explicitly, the low thermal emission polyacrylamide (PAM) hydrogel ensures efficient heat confinement and water suction which also acts as thermogalvanic quasi-solid electrolyte. While the hierarchical micro-nano copper oxides structure plays a dual role of broadband light absorptive solar thermal material and high electrochemical surface area thermal/electrical conductive (thermogalvanic) electrodes. Meanwhile, the judicious introduction of polydimethylsiloxane (PDMS) polymer film serves as multifunctional coating for optical trapping with enhanced internal multiple reflection off the hierarchical micro- and nanostructure to impede light escape and at the same time provides passivation against rugged operating conditions. Consequently, an integrative prototype is proven to effectively suppress the rapid heat losses and localize the photothermal heat at upper air-water interface to boost water evaporation and create large temperature gradient for thermogalvanic voltage/current generation, suggesting a symbiotic and pragmatic strategy of solar-driven freshwater and thermoelectricity generation. Furthermore, the built-in features of the prototype are to better respond to the demands of the maximizing solar energy and land-use, minimal environmental impact, modularity of infinitely arrayed, and collapsible structures as well as continuous outdoor deployment.

2. Results and Discussion

The layer-by-layer assembly of an integrative photothermal evaporator/thermogalvanic cell is schematically depicted in Figure 1. Namely, the symmetrically designed sandwich hybrid device consists of bilateral copper oxide/copper foil (CuO/ Cu foil) with PDMS and PAM hydrogel coatings, and cupric sulfate-PAM hydrogel electrolyte occupying the middle section. The multilayered PDMS/CuO/Cu foil composite is essentially adopted as broadband light absorber contributing to efficient photothermal conversion, as well as serving as thermogalvanic electrodes. The PAM hydrogel coating on PDMS/CuO/Cu foil facilitates a constant supply of water. The middle hydrogel electrolyte is sealed by PDMS to ensure good contact with the Cu foils on both sides and prevent it from dehydrating. When exposed to simulated solar irradiation, the mixed CuO microand nanostructure/PDMS coating absorbs light to induce photothermal conversion for dual purposes evaporation of water contained in the upper PAM hydrogel, and establishing a temperature gradient across the low thermal-conductive PAM hydrogel electrolyte to trigger the temperature-dependent redox reaction of copper/cupric sulfate to generate a thermogalvanic voltage between opposite electrodes. Meanwhile, self-restoring redox cycling is further proposed on the account of the



Figure 1. Schematic drawing of the designed integrative photothermal evaporator/thermogalvanic cell.

www.advancedsciencenews.com

IDVANCED

S

FUNCTIONAL



Figure 2. a) Schematic illustration for the multilayer structure and functions of PDMS/CuO/Cu foil. b) SEM image of the CuO micro-/nanostructure in CuO/Cu foil. c) Temperature and specific capacitance of CuO/Cu foils with various etch time. d) Cross-sectional SEM image of PDMS/CuO/Cu foil. e) UV-vis–NIR reflection spectra of PDMS/CuO/Cu foil, CuO/Cu foil, and Cu foil, f) corresponding temperature evolution, and g) infrared images under simulated one sun light irradiation. h) Cross-sectional SEM image of PPCC. i) SEM image of the top salt-template PAM aerogel in PPCC. j) UV-vis–NIR reflection and k) transmission spectra of PPCC, hydrogel–PPCC, and PAM aerogel/hydrogel.

symmetrical device construction to resolve the consumption of Cu-based electrodes.

The solar absorbing/photothermal layer is prepared by incorporating PDMS and CuO micro- and nanostructure onto Cu foil. Figure 2a illustrates the multilayer structure of PDMS/ CuO/Cu foil, the synthetic process includes in situ etching formation of CuO microflowers on the Cu foil substrate in mixed solution of sodium hydroxide and ammonium persulfate, follow by PDMS knife coating. Visually noticeable color changes to the samples can be seen with sequential steps (Figure S1a-c, Supporting Information), and verified by X-ray diffraction patterns (Figure S1d, Supporting Information). The time parameter is taken into account to explore the etching levels of Cu foils as the various resultant morphologies of the CuO layer on Cu foil are studied using scanning electron microscopy (SEM). As shown in Figure 2b and Figure S2 (Supporting Information), surface textures evolve from nanosheets to increasingly flower-like structures from nanoscale to micro- and nanoscale with the reaction time. Of particular note is that the individually and loosely interconnected CuO microflowers are seen to cluster and build up on the Cu substrate, engendering a highly irregular and macroporous structure. Optical properties of the samples with different surface textures are then examined by ultraviolet-visible-near-infrared (UV-vis-NIR) diffuse reflectance spectroscopy (Figure S3a, Supporting Information). The degree of reflection is almost consistent with morphology evolution over time. All samples with etching time longer than 12 h have full absorption in UV and visible regions. The 72 h sample exhibits the lowest light reflectance (≈9-20%) in NIR region, compared to that of 24 h (≈15–30%), 48 h (≈12–24%), and 120 h (\approx 9–20%). The extraordinary degree of matching between the structures and light absorption ability can be attributed to the scattering of light by the hierarchical micro- and nanoscale structures that increase the optical path length via multiple reflections.^[38,39] Under simulated one sun irradiation (100 mW cm⁻²), the samples (48-120 h) heats up rapidly to more than 70 °C (Figure S3b, Supporting Information), indicating high-photothermal conversion efficiency. On the other hand, a thermogalvanic cell has a high requirement for electrochemical specific surface area (ECSA) of the electrodes, which is evaluated by measuring the pseudocapacitance behaviors of various samples. Figure S4a–f of the Supporting Information presents a variation of specific capacitance of samples versus scan rates. The highest value is obtained at 12 h and then decreases with increasing etching time, exhibiting a rapid decline especially at etching times as long as 72 and 120 h.

The CuO/Cu foil (48 h) is selected for the subsequent PDMS knife coating process along with the thickness studies (Figure S4h, Supporting Information) after careful consideration of photothermal conversion and ESCA requirements (Figure 2c). The cross-sectional SEM image (Figure 2d) shows excellent conformity of the PDMS coating to the CuO/Cu foil. The PMDS/ CuO/Cu foil shows a decrease in the UV-vis-NIR diffuse reflectance (Figure 2e), and temperature increment from 71 to 87 °C (Figure 2f), whereas the PDMS itself exhibits negligible light absorption (Figure S5, Supporting Information) and slight temperature change from 22 to 30 °C (Figure 2f). Hence, the enhancement could be attributed to a more efficient capturing of the incoming solar energy of the PMDS/ CuO/Cu over Cu or CuO/Cu sample. Essentially, the favorable refractive index of the PDMS in part promotes internal reflection of the infrared light and retards light escape,^[40,41] while the lining and coverage of the inner spaces of the hierarchical CuO micro- and nanostructures creates numerous interfaces that further enable multiple reflections with longer optical path length for light absorption. The much higher and more uniform temperature distribution shown in the infrared image of PDMS/CuO/Cu foil in comparison with CuO/Cu foil and Cu foil (Figure 2g) provides a complementary evidence to this conjecture. PDMS coating can also reduce optical losses of Cu foil and Ni foam caused by the poor trapping of weakly absorbed long-wavelength light, and subsequent temperature increase and homogeneous heat distribution under sun irradiation (Figure S6c-e, Supporting Information) is anticipated. Above all, the superior photon absorption and solar thermal conversion accompanied by high ECSA of PDMS/CuO/Cu foil lay the foundation for the following water evaporation and thermogalvanic cell work.

For the purpose of water wicking for evaporation and establishing large temperature gradient across the integrative cell, PAM hydrogel is employed. A salt template-assisted gelation and freeze-drying method is used to prepare PAM aerogel with tunable surface morphologies, and recovery to hydrogel for water supply and as quasi-solid electrolyte when required. The PAM aerogel is then bonded to PDMS/CuO/Cu foil using half cured PDMS as binder to construct PAM/PDMS/CuO/Cu foil (PPCC). The surface morphology and structure of PPCC and PAM aerogel synthesized without salt template are also examined using SEM. The cross-sectional SEM images of PPCC in Figure 2h,i show perfect integration of the top PAM and PDMS layers of PPCC, with the PDMS binder taking up a very small fraction of porous structure in PAM aerogel at the joint interface, and the thickness of PAM layer is about 500 µm. Both the PAM aerogels synthesized with and without salt template presents a macroporous structure with rugged surface topography (Figure S7a-c, Supporting Information). However, the salt template-assisted PAM aerogel possesses micro- and nanoscale pores nested within the larger pores in the salt template-assisted PAM aerogel. Such hierarchical structure may

be resulted from the interpenetration of salt solution into the PAM, following that, the low temperature crystallization of salt templates further extrudes PAM chains, and the final process of template removal and refreeze-drying results in the extra pores formation. Simulations of temperature distributions shown in Figure S7e,f of the Supporting Information indicate that surface roughening can increase the heat confinement and lower the energy loss compared to that of the smooth surface. Furthermore, tailoring surface topography of hydrogel-based solar evaporator into micro-/nanoscale could shape the surface envelope or front of the evaporation film that has a strong impact on the water evaporation behavior.^[42-44] Fourier transform infrared spectroscopy (Figure S7d, Supporting Information) shows that the additional salt template only influences the surface instead of changing the original polymeric skeleton, suggesting strong chemical bonding between polymer molecules and water molecules, with the complex microstructure giving rise to a better water capillary effect. Therefore, water pumping capability can be enhanced to improve water and ion exchange without loss in water retention. Taken in water, the mass ratio (W_{H_2O-ab}/W_{PAM}) for salt template-assisted PAM aerogel can rapidly reach up to more than 35-fold compared to that without salt template (less than tenfold), besides, salt template derived complex porous structure also promotes ion exchange with lower electrochemical impedance (Figure S8, Supporting Information). From the solvent exchange experiments (Figure S9, Supporting Information), it is evident that the PAM aerogel can easily wick water within seconds (colored with dyes for visualization), as well as release ions immediately. To evaluate the light absorption of PAM aerogel/hydrogel and PPCC (absorbing water named as hydrogel-PPCC), UV-vis-NIR spectra including reflectance and transmittance are collected for analysis (Figure 2j,k). After water absorption, the PAM hydrogel presents excellent light transmittance in visible region (~85%) and about 60% absorption of near-infrared spectrum compared to original PAM aerogel. Seemingly, the hydrogel-PPCC has a broadband absorption in full spectrum, implying efficient solar harvesting capability.

To test the integrative performance of steam and thermogalvanic generation, the PAM hydrogel electrolyte and PPCC layer-by-layer assembly with sandwich-like construction is built as PPCC cell, as shown in Figures 1 and 3a. Unique features of each part contributes to the several distinct characteristics inherent in the cell that is designed for practical application, including low density and hydrophobicity for its free floating at water-air interface, high elasticity, and mechanical strength for a complete recovery after undergoing various deformations (Figure S10, Supporting Information). Another essential factor for localizing heat at air-water interface is the superior thermal insulation property that is necessary for minimizing heat loss. Being part of the cell, the intrinsic low thermal conductivity PAM polymer skeleton and porous structure contributes significantly to its excellent thermal insulation. Evidently, Figure S11a of the Supporting Information presents a high temperature difference of about 26 °C between the bottom and top of PAM aerogel when placed on a heating source. In addition, when the PPCC cell and hydrogel-PPCC itself are simultaneously removed from hot water (\approx 45 °C), the cell takes a longer time to cool down to room temperature

www.advancedsciencenews.com

IDVANCED







Figure 3. a) Schematic illustration of photothermal water evaporation measurement. b) Temperature evolution of samples with different layers under one sun irradiation over time. c) Corresponding infrared images over time of the PPCC cell. d) Evaporation rates of samples with different layers. e) Corresponding conversion efficiencies. f) Evaporation rates and efficiencies under different solar intensities. g) Evaporation rates of the PPCC cell and its contrast under different salinities (inset: photographs of salt deposition with (left)/without (right) using PAM hydrogels in the cells). h) Stability and reusability of the PPCC cell for solar vaporization.

compared to the hydrogel–PPCC (Figure S11b,c, Supporting Information). Therefore, the rational integrative assembly of a solar absorber for photothermal steam generation and a thermocell for thermoelectricity generation achieves the necessary insulation properties to realize hotspot at air–water interface and large temperature gradient against the underlying bulk water.

Taking into account the desirable optical, thermal, and water management properties implemented into one integrative cell, we started with the initial investigation of its interfacial solar-driven water evaporation. For comparison, we also prepare similar cells by replacing PDMS/CuO/Cu foil with CuO/ Cu foil or Cu foil or PDMS film in PPCC, which are devoted as PAM/CuO/Cu foil, PAM/Cu foil, and PAM/PDMS, respectively. Upon exposure to simulated solar irradiation (one sun), temperatures of the evaporation surface of all these integrative cells assembled by various layers, and bulk water over time are monitored using infrared imaging. As shown in Figure 3b, both integrative cells and bulk water present an immediate rise in surface temperature. Integrative cells with PPCC, PAM/CuO/ Cu foil, or PAM/Cu foil can reach a steady state equilibrium temperature in about 5-10 min, while temperatures of integrative cell with PAM/PDMS and bulk water increase much slowly to about 28 and 26 °C after 30 min, respectively. Obviously, with an optimized solar absorber (PDMS/CuO/Cu foil), the highest surface temperature can reach up to \approx 38.9 °C, which is ≈12.9 °C higher than that of bulk water. Infrared images of the surface of PPCC cell along with exposure time of 0, 5, 10, and 30 min are shown in Figure 3c, confirming the confinement of the thermal energy at the air-water surface. Subsequently, high steam flux generation and photothermal conversion efficiency can be expected.





The evaporation rates of all integrative cells and bulk water under one sun are then quantified by recording the weight loss of water point-by-point with constant time interval. As shown in Figure 3d, the evaporation rates for PPCC, PAM/CuO/ Cu foil, PAM/Cu foil, or PAM/PDMS-based integrative cells, and blank water, are 1.33, 0.93, 0.51, 0.26, and 0.16 kg m⁻² h^{-1} , respectively, which correspond to the conversion efficiencies of 91.41%, 63.78%, 35.32%, 17.69%, and 10.83% (Figure 3e) calculated according to Equations (S1) and (S2) of the Supporting Information. Water evaporation rates and corresponding solar thermal conversion efficiencies of the PPCC cell under other constant illuminations of various sun power are also measured and recorded in Figure 3f and Figure S12b (Supporting Information), which prove its favorable solar tolerance. The individual hydrogel-PPCC as a membrane evaporator is further evaluated, by contrast, it exhibits an evaporation rate of 0.56 kg m⁻² h⁻¹ under the same condition (Figure S12c, Supporting Information). In addition, a lower evaporation rate of 1.22 kg m⁻² h⁻¹ is obtained on the cell assembled using salt-template free PAM. The significantly higher evaporation rate and energy efficiency of the PPCC cell than that of all control samples confirm advantages from the efficient solar absorption and photothermal conversion of PDMS/CuO/Cu foil, the crucial insulation role of an integrative cell for hot localized solar thermal conversion, and tailored surface structure of PAM for enhanced evaporation.

To further demonstrate the potential of salt-rejection for solar desalination, a highly concentrated brine solution (with a salinity of 5, 10, 15, and 20 wt%) is used. The water evaporation rate is noted to be almost consistent after 180 min continuous tests in all these brine solutions (Figure 3g). This essential property is also visually observed under one sun irradiation, where the PPCC cell with PAM hydrogel layer remains clear,

showing a uniform black color, without salt deposits (Figure 3g inset). When the PAM was replaced with tissue as contrast for comparison (Figure S13, Supporting Information), it can be seen that severe salt crystallization fouls the surface and gradually decreases the evaporation rate in high-concentration salt solution. The salt-rejection ability is attributed to sufficient water and ion exchange across the hydrophilic and highly macroporous PAM hydrogel, and the hydrophobic PDMS may further curb the precipitation of crystalline salt (Figure S14, Supporting Information). The PDMS passivation layer validates chemical and structural resistance toward radical pH (1 and 13) and environmental exposure (Figure S15, Supporting Information). Hence, a practical solar desalination or wastewater purification without extra cleaning treatment is assured on this PPCC cell. It is also worth pointing out the negligible fluctuation in water evaporation performance over reusability and recycling tests is crucial for operation in real conditions due to the diurnal variation and position shift (Figure 3h). Together, the results discussed above consistently demonstrate efficient optical, thermal, and water management of the optimized layerby-layer assembled composite film for localized photothermic interfacial evaporation.

The PPCC cell is then used as a thermogalvanic cell for thermoelectricity generation to collect low-grade solar heat, utilizing the temperature gradient across the cell schematized in Figure 1 and Figure S16a (Supporting Information). The intrinsic activity of this PPCC cell is first measured. When a series of temperature differences is applied against the PPCC cell, a linear relation temperature-dependent thermogalvanic voltage/current is generated accordingly. Open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}) of the PPCC cell are recorded in **Figure 4**a. The thermoelectrochemical Seebeck coefficient is



Figure 4. a) Open-circuit thermogalvanic voltages of the PPCC cell at different temperatures. b) Temperature profiles of the upper and bottom surfaces, open-circuit voltage and short-circuit current of the PPCC cell under chopped one sun illumination (inset: temperature difference between two surfaces). c) Discharge polarization curves and related power densities of the thermogalvanic cells using Cu foil (removing one side CuO layer in CuO/Cu foil) or CuO/Cu foil as electrodes. d) Schematic diagram for self-restoring of the PPCC cell. e) Open-circuit voltage of the cell with 1 cycle rotation. f) Open-circuit voltages under different solar intensities and different bulk water temperatures. g) Water evaporation rates and thermogalvanic V_{oc} of the PPCC cell in simulated seawater for a long time (insets: typical solar evaporation and thermogalvanic behaviors for 30 days).

IDVANCED

calculated to be about 1.2 mV K⁻¹, which is similar to previously reported Cu⁰/Cu²⁺ based thermocell.^[45,46] Pertaining to the high conductive Cu substrate and chemical etching induced high ECSA, the thermogalvanic short-circuit current density can reach \approx 0.9 A m⁻² at a temperature difference of 10 °C (Figure S16b, Supporting Information).

The free-floating feature of the PPCC cell and its hydrophobic PDMS coating allows only the bottom portion of the cell to be submerged instead of the entire cell. Consequently, the upper solar absorption layer (also functioning as a thermogalvanic electrode) exhibits a high temperature gain whilst the sandwiched PAM hydrogel serves as thermal insulation and electrolyte medium that delay heat diffusion as opposed to the bottom electrode that is cooled by bulk water. This favorably creates a large temperature gradient across the cell. As a matter of course, Seebeck effect triggered by this temperature difference is materialized. As shown in Figure 4b upon exposure to an on/ off cycle under one sun irradiation, both temperature profiles of the top and bottom of the cell present an instantaneous rise and a temperature difference (ΔT). The maximum ΔT is about 8.7 °C, the $V_{\rm oc}$ closely correlates to the ΔT and reaches up to \approx 10.3 mV. Photosensitivity of the temperature and V_{oc} profiles can obviously be seen to associate to the on/off light source, thus verifies a photothermal mediated thermoelectric generation. The temperature gradient and corresponding V_{oc} of the cell exposed to different solar densities (50, 150, and 200 mW cm⁻²) offer further proofs (Figure S19a-c, Supporting Information), i.e., ΔT of 6.1, 13.0, and 15.5 °C, and respective V_{oc} of 7.5, 14.1, and 17.0 mV. Notably, the ΔT and associated $V_{\rm oc}$ are almost linearly related to the input solar densities. Moreover, the thermogalvanic cell shows a longevity and excellent cycle stability for continuous power generation (Figure S19d, Supporting Information). The discharge polarization curves and related power densities of the cells using Cu foil (removing one side CuO layer without PDMS coating in PDMS/CuO/Cu foil) or CuO/Cu foil (directly using PDMS/CuO/Cu foil) electrodes presented in Figure 4c reveal that the output peak power densities are 1.01 and 1.57 mW m⁻² under one sun, respectively, attributed to the much higher ECSA of CuO hierarchical structures. In view of the thermoelectricity generation based on redox Cu⁰/ Cu²⁺, constant consumption of Cu on the cold side may inevitably result in breakdown of the integrative cell in severe case. To resolve this issue, self-restoring electrochemical redox reaction is proposed, leveraging on the purposefully design symmetric assembly (Figure 4d). As shown in Figure 4e, an alternatively positive and negative $V_{\rm oc}$ plot is generated with each rotation, and both have an absolute value around 10 mV. The structure of electrodes with repeated deposition of copper ions via mechanical rotation is then investigated. SEM images of the electrodes with various rotation time interval and repeated cycles (Figures S17 and S18, Supporting Information) present the structure recovery, which validates the self-restoring strategy. In a natural environment, the wind and water oscillation and fluctuation of seiche and tide of various water bodies can potentially be harnessed to rotate the device, as such turning these mechanical powers into electrochemical energy.

The aforementioned thermoelectric properties are strongly dependent upon the temperature difference between the upper solar absorber and bottom bulk water, which is inevitably affected by the temperature increase of the limited volume of static water under continuous light irradiation. Clearly, this is different from the open outdoor environment, e.g., sea, river, etc. To simulate the actual scenarios of natural water bodies temperature which generally remains fairly constant, a circulating water bath with temperatures of 30, 25, 20, and 15 °C is introduced. The temperature profiles and gradients are recorded in Figure S20a of the Supporting Information. Despite lower temperature achieved on the top surface under the influence of a lower temperature circulating water, a larger temperature difference of 14.8 °C can be realized, thus leading to a higher thermogalvanic voltage of 16.6 mV at a flowing water temperature of 15 °C under one sun. Thermogalvanic voltages of 13.4, 10.9, and 9.0 mV were obtained for flowing water temperatures of 20, 25, and 30 °C, respectively (Figure 4f; Figure S20c, Supporting Information). The photothermal evaporation rate in this case is also monitored. As shown in Figure S20d of the Supporting Information, the evaporation rates decline with decreasing circulating water temperature, and the corresponding values of 1.69, 1.44, 1.20, and 1.07 kg m⁻² h⁻¹ at 30, 25, 20, and 15 °C. As shown in Figure 4g, the PPCC cell presents a stable water evaporation rate and thermogalvanic V_{oc} exposure to one sun irradiation in simulated seawater as long as 30 days. Together, the data indicate a synergetic production of clean water and electrical energy based on an integrative solar absorber and thermocell for extensive solar energy utilization, and both present competitive performances (Tables S1–S3, Supporting Information).

Practical outdoor water evaporation and thermogalvanic experiments based on the PPCC cells are then performed to prove the concept of concurrent clean energy-water harvesting under natural sunlight conditions. An array of modular PPCC cells model with active area of 9×2 cm $\times 2$ cm, assembled in series, self-floated on a simulated seawater (salinity of 3.5 wt%) was placed in a transparent pyramid solar prototype with condensate collection troughs and bottle (Figure 5a). A real-time monitoring of solar flux, model surface and ambient temperatures, water evaporation rate, and output voltage data are conducted. The natural sunlight presents time-dependent solar intensity variability (≈200-800 W m⁻², Figure 5e, black line) from 11:00 to 14:00 (19 October 2019). Localized solar thermal conversion is shown by the infrared image of Figure 5b with concurrent temperature rise of the model surface up to ≈ 38 °C (Figure 5e, red line), which enables water evaporation rate of \approx 1.12 kg m⁻² h⁻¹ (Figure 5e, blue line), which is close to the prior solar evaporation measurements (Figure 3f). The collected condensate water droplets during vaporizing process can be observed on pyramid walls, troughs, and collecting bottle (Figure 5c). The significantly reduced concentrations of four primary ions (Na⁺, Mg²⁺, K⁺, and Ca²⁺) as evaluated by inductively coupled plasma spectroscopy evidently indicate the high quality of the collected water (Figure 5d). Simultaneously, thermogalvanic voltages are recorded every 10 min (Figure 5e, brown line), which seemingly follow the trend of the modeled surface temperature. The maximum value can reach up to \approx 83.7 mV, equivalent to 9 \times 9.3 mV, proving the scheme of tandem constructs for higher output voltage. Furthermore, the highlight features include large scale facile preparation, excellent flexibility/modularity, and free-floatage system (Figure 5f,g;





Figure 5. a) Photograph of the solar still (inset: multimeter for recording thermogalvanic voltages) and b) infrared image of the 3×3 tandem cells in nature sunlight outdoor test after 3 h sun irradiation. c) The photograph of condensate water in the troughs of the solar still and d) corresponding ion concentration analysis of the collected water after desalinization. e) The solar intensity spectra (black), evaporation mass loss (blue), thermogalvanic voltages (brown), and synchronous temperature changes of the tandem cells surface (red) and ambient air (cyan) under the sun from 11:00 to 14:00 (19 October 2019) at National University of Singapore, Kent Ridge campus. f,g) Photograph for the large-scale preparation of the multilayer foil and following tandem cells. h) Schematic diagram and i) photographs of the prototype floating on natural water.

Figure S21d–f, Supporting Information). Finally, a larger foldable and portable prototype (Figure 5h; Figure S21a–c, Supporting Information) for solar energy water purification and electricity harvesting is designed, highly feasible for different application scenarios, particularly in varied field water bodies (rivers, lakes, seas, ponds, etc.). As shown in Figure 5i, visible condensate droplets on walls and water in the collecting bag along with 0.225 V multimeter display, demonstrate successful deployment of the sustainable, on-site hybrid water-energy technology.

3. Conclusion

In summary, we have successfully demonstrated a hybrid photothermal steam and energy generator on a layer-bylayer assembled integrative evaporator/thermogalvanic cell for comprehensive utilization of renewable solar energy. The multilayered PDMS/CuO/Cu foil possesses desirable attributes such as broadband light absorption, photothermal conversion, chemical stability under various operating conditions, high electrical conductivity, and electrochemical specific surface area manifest as robust solar absorber and thermogalvanic electrode. With the judicious introduction of PAM hydrogel to assemble the cell, its desired properties including rapid water suction and ion exchange, high light transmission, and thermal insulation promise an efficient optical, heat, and water management well-aligned toward an integrative cell. An evaporation rate of 1.33 kg m^{-2} h^{-1} , conversion efficiency up to ≈91.4%, and synchronous thermogalvanic power output as high as ≈1.6 mW m⁻² are achieved under one sun. Moreover, the integrative cell exhibits high mechanical stability and resistance against demanding water environment including high salinity, universal acidity, and alkalinity conditions, endowing its enormous potential for seawater desalination and water purification. Localized photothermal water evaporation and thermogalvanic energy generation and their extension for a scalable clean water and power production under ambient outdoor conditions using diverse prototypes are also demonstrated. Such integrative evaporator/thermogalvanic cell and modular deformable assemble may open new avenues for coproduction of clean water and electricity, well poised for long sea-voyage and remote islands deployment.

FUNCTIONAL

www.afm-journal.de

Supporting Information

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

SCIENCE NEWS _____ www.advancedsciencenews.com

DVANCED

Acknowledgements

This work was supported by the Ministry of Education Singapore (MOE), R-263-000-D08-114, R-263-000-C85-112, and R-263-000-D18-112.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

integration, modular, photothermal, steam generation, thermogalvanic

Received: March 31, 2020 Revised: April 25, 2020 Published online: June 29, 2020

- P. J. J. Alvarez, C. K. Chan, M. Elimelech, N. J. Halas, D. Villagran, Nat. Nanotechnol. 2018, 13, 634.
- [2] C. Chen, Y. Kuang, L. Hu, Joule 2019, 3, 683.
- [3] P. Tao, G. Ni, C. Song, W. Shang, J. Wu, J. Zhu, G. Chen, T. Deng, *Nat. Energy* 2018, 3, 1031.
- [4] Y. Yang, X. Yang, L. Liang, Y. Gao, H. Cheng, X. Li, M. Zou, A. Cao, R. Ma, Q. Yuan, X. Duan, *Science* **2019**, *364*, 1057.
- [5] X. Yang, Y. Yang, L. Fu, M. Zou, Z. Li, A. Cao, Q. Yuan, Adv. Funct. Mater. 2018, 28, 1704505.
- [6] D. J. Xue, S. C. Liu, C. M. Dai, S. Chen, C. He, L. Zhao, J. S. Hu, L. J. Wan, J. Am. Chem. Soc. 2017, 139, 958.
- [7] P. Zhang, J. Li, L. Lv, Y. Zhao, L. Qu, ACS Nano 2017, 11, 5087.
- [8] C. Ma, J. Yan, Y. Huang, C. Wang, G. Yang, Sci. Adv. 2018, 4, eaas9894.
- [9] T. Gao, Y. Li, C. Chen, Z. Yang, Y. Kuang, C. Jia, J. Song, E. M. Hitz,
 B. Liu, H. Huang, J. Yu, B. Yang, L. Hu, *Small Methods* 2019, *3*, 1800176.
- [10] J. Yao, Z. Zheng, G. Yang, Nanoscale 2018, 10, 2876.
- [11] X. Wang, Q. Liu, S. Wu, B. Xu, H. Xu, Adv. Mater. 2019, 31, 1807716.
- [12] X. Zhang, H. Ye, B. Xiao, L. Yan, H. Lv, B. Jiang, J. Phys. Chem. C 2010, 114, 19979.
- [13] Z. Deng, J. Zhou, L. Miao, C. Liu, Y. Peng, L. Sun, S. Tanemura, J. Mater. Chem. A 2017, 5, 7691.
- [14] L. Zhu, M. Gao, C. K. N. Peh, G. W. Ho, Mater. Horiz. 2018, 5, 323.
- [15] M. Ye, J. Jia, Z. Wu, C. Qian, R. Chen, P. G. O'Brien, W. Sun, Y. Dong, G. A. Ozin, *Adv. Energy Mater.* 2017, *7*, 1601811.
- [16] H. C. Yang, Z. Chen, Y. Xie, J. Wang, J. W. Elam, W. Li, S. B. Darling, Adv. Mater. Interfaces 2019, 6, 1801252.
- [17] Y. Li, T. Gao, Z. Yang, C. Chen, W. Luo, J. Song, E. Hitz, C. Jia, Y. Zhou, B. Liu, B. Yang, L. Hu, *Adv. Mater.* **2017**, *29*, 1700981.
- [18] H. Liu, Z. Huang, K. Liu, X. Hu, J. Zhou, Adv. Energy Mater. 2019, 9, 1900310.



www.afm-journal.de

- [19] Y. Xu, J. Ma, Y. Han, J. Zhang, F. Cui, Y. Zhao, X. Li, W. Wang, ACS Sustainable Chem. Eng. 2019, 7, 5476.
- [20] A. Politano, P. Argurio, G. Di Profio, V. Sanna, A. Cupolillo, S. Chakraborty, H. A. Arafat, E. Curcio, Adv. Mater. 2017, 29, 1603504.
- [21] W. Xu, X. Hu, S. Zhuang, Y. Wang, X. Li, L. Zhou, S. Zhu, J. Zhu, Adv. Energy Mater. 2018, 8, 1702884.
- [22] F. Zhao, X. Zhou, Y. Shi, X. Qian, M. Alexander, X. Zhao, S. Mendez, R. Yang, L. Qu, G. Yu, *Nat. Nanotechnol.* **2018**, *13*, 489.
- [23] X. Zhou, F. Zhao, Y. Guo, Y. Zhang, G. Yu, Energy Environ. Sci. 2018, 11, 1985.
- [24] C. Chen, Y. Li, J. Song, Z. Yang, Y. Kuang, E. Hitz, C. Jia, A. Gong, F. Jiang, J. Y. Zhu, B. Yang, J. Xie, L. Hu, *Adv. Mater.* **2017**, *29*, 1701756.
- [25] J. Yao, G. Yang, J. Mater. Chem. A 2018, 6, 3869.
- [26] H. Ren, M. Tang, B. Guan, K. Wang, J. Yang, F. Wang, M. Wang, J. Shan, Z. Chen, D. Wei, *Adv. Mater.* 2017, *29*, 1702590.
- [27] Y. Shi, R. Li, Y. Jin, S. Zhuo, L. Shi, J. Chang, S. Hong, K.-C. Ng, P. Wang, *Joule* 2018, 2, 1171.
- [28] Y. Yang, X. Yang, L. Fu, M. Zou, A. Cao, Y. Du, Q. Yuan, C.-H. Yan, ACS Energy Lett. 2018, 3, 1165.
- [29] Y. Yang, H. Zhao, Z. Yin, J. Zhao, X. Yin, N. Li, D. Yin, Y. Li, B. Lei, Y. Du, W. Que, *Mater. Horiz.* **2018**, *5*, 1143.
- [30] C. Li, D. Jiang, B. Huo, M. Ding, C. Huang, D. Jia, H. Li, C.-Y. Liu, J. Liu, Nano Energy 2019, 60, 841.
- [31] X. Gao, H. Ren, J. Zhou, R. Du, C. Yin, R. Liu, H. Peng, L. Tong, Z. Liu, J. Zhang, Chem. Mater. 2017, 29, 5777.
- [32] J. Yao, Z. Zheng, G. Yang, Nanoscale 2017, 9, 16396.
- [33] R. Hu, B. A. Cola, N. Haram, J. N. Barisci, S. Lee, S. Stoughton, G. Wallace, C. Too, M. Thomas, A. Gestos, M. E. Cruz, J. P. Ferraris, A. A. Zakhidov, R. H. Baughman, *Nano Lett.* **2010**, *10*, 838.
- [34] D. Kraemer, B. Poudel, H.-P. Feng, J. C. Caylor, B. Yu, X. Yan, Y. Ma, X. Wang, D. Wang, A. Muto, *Nat. Mater.* 2011, *10*, 532.
- [35] L. Xu, Y. Xiong, A. Mei, Y. Hu, Y. Rong, Y. Zhou, B. Hu, H. Han, Adv. Energy Mater. 2018, 8, 1702937.
- [36] P. Yang, K. Liu, Q. Chen, X. Mo, Y. Zhou, S. Li, G. Feng, J. Zhou, Angew. Chem., Int. Ed. 2016, 55, 12050.
- [37] T. Kim, J. S. Lee, G. Lee, H. Yoon, J. Yoon, T. J. Kang, Y. H. Kim, Nano Energy 2017, 31, 160.
- [38] S. Hong, Y. Shi, R. Li, C. Zhang, Y. Jin, P. Wang, ACS Appl. Mater. Interfaces 2018, 10, 28517.
- [39] S. Thongrattanasiri, F. H. Koppens, F. J. G. De Abajo, Phys. Rev. Lett. 2012, 108, 047401.
- [40] A. Llobera, S. Demming, R. Wilke, S. Buttgenbach, Lab Chip 2007, 7, 1560.
- [41] S. Manzoor, Z. J. Yu, A. Ali, W. Ali, K. A. Bush, A. F. Palmstrom, S. F. Bent, M. D. McGehee, Z. C. Holman, *Sol. Energy Mater. Sol. Cells* **2017**, *173*, 59.
- [42] Y. Guo, F. Zhao, X. Zhou, Z. Chen, G. Yu, Nano Lett. 2019, 19, 2530.
- [43] C.-C. Hsieh, S.-C. Yao, Int. J. Heat Mass Transfer 2006, 49, 962.
- [44] M. Pais, L. Chow, E. Mahefkey, J. Heat Transfer 1992, 114, 211.
- [45] A. Gunawan, H. Li, C.-H. Lin, D. A. Buttry, V. Mujica, R. A. Taylor, R. S. Prasher, P. E. Phelan, Int. J. Heat Mass Transfer 2014, 78, 423.
- [46] S. W. Lee, Y. Yang, H. W. Lee, H. Ghasemi, D. Kraemer, G. Chen, Y. Cui, Nat. Commun. 2014, 5, 3942.