Supplementary Information (SI) for Journal of Materials Chemistry A.

High-performance biomass-based solar-thermal hydrogel based on silkworm excrement for water evaporation and thermoelectric integration application

Shuqing Ao[a], Zhifei Chen[b], Haoyang Chen[b], Liuke Zhang[b], Yanan Wang[a], Yingyuan Zhang[a], Tao Jia*[a], Gaolei Xi*[b], Tai Peng*[c]

a. Key Laboratory of Forest Plant Ecology, Ministry of Education, Engineering Research Center of Forest Bio-Preparation, College of Chemistry, Chemical Engineering and Resource Utilization, Northeast Forestry University, Harbin 150040, China

b. Technology Center for China Tobacco Henan Industrial Limited Company, Zhengzhou, 450000, China

c. School of Materials Science & Engineering, Jiamusi University, Jiamusi, 154007, China.

Preparation of silkworm excrement hydrogels: Silkworm excrement hydrogel (SE/H) was prepared by stirring 8% (w/v) PVA (weight-average molecular weight: 205000) and 50% GLUT at a ratio of 25:1, and fixed silkworm excrement powder was mixed. Stir them at 100°C for 2 hours, and then cool to room temperature. After that, add hydrochloric acid and stir the sample again for 2 hours to promote cross-linking between PVA chains. Then pour the fully mixed solution into the mold and solidify at room temperature overnight for molding. Subsequently, the obtained hydrogel is moved to -20 °C and frozen for about 24 hours, and then thawed at room temperature for 12 hours for three consecutive cycles to prepare a physical cross-linking structure for further experiments.

General information: The UV-vis-NIR absorption spectra of silkworm excrement and mulberry leaves solid powder were recorded by the Shimadzu UV-2550 spectrophotometer.

Photothermal experiments: SEM (EM-30plus) was used to observe the morphology of silkworm excrement hydrogels. Infrared thermal imager (TESTO-869) was used to record the change of temperature. The experiments of water evaporation and thermoelectric generation were carried out with xenon Cell-S500/350 light source (AM 1.5 G spectral filter). TES1-24103 was used as a thermoelectric device, and the open-circuit voltage data was obtained by FLUKE 8846A system.

Solar steam generation experiments: SE/H rests on a container that is filled with water. The sunlight, generated by a solar simulator with an optical filter for the standard AM 1.5 G spectrum (CEL-S500/350), irradiated at the sample under specific optical concentrations. The weight loss of water was measured by an electronic mass balance and the temperature over the process was recorded by an IR thermal camera. The energy conversion efficiency was determined according to previous methods.

Solar temperature difference power generation: Commercial thermoelectric generator (TESTO-869, long 40 mm, wide 40 mm, high 3.6 mm) was selected for power generation. The SE/H on the upper surface of the thermoelectric sheet, and the lower part was connected with cold water. Thermoelectric open circuit voltage (V_{OC}) were measured and recorded by Keithley 6514 system electrometer instrument. The subsequent power generation was carried out on the 1, 2, and 5 kW m^{-2} respectively, and the surface temperature was collected and recorded by infrared thermal imager.

Calculation of the photothermal conversion efficiency: The 5 mg silkworm excrement powder was dispersed in 1 mL water with an insulating layer and illuminating the solution with simulated solar light. The temperature of the solution was recorded using a thermal imaging camera upon simulated solar light irradiation for 20 minutes and energy conversion efficiency (η) was calculated as the following formula:

$$\eta = \frac{Q}{E} = \frac{Q_1 - Q_2}{E}$$

Where Q refers to the thermal energy generated (i.e., $Q = Q_1 - Q_2$), Q_1 is the thermal energy generated of silkworm excrement and Q_2 is the thermal energy generated of pure water. E refers to the total energy of the incident light. Q is determined by the heat capacity (C), density (ρ), volume (V) and ΔT over the period of irradiation of the solution; E is determined by the power (P) of the incident light, the irradiation area (S) and irradiation time (t). Therefore, the specific formula is as follows:

$$Q_1 = Cm\Delta T_1 = C\rho V\Delta T_1$$

$$Q_2 = Cm\Delta T_2 = C\rho V\Delta T_2$$

$$E = PSt$$

In this work, since samples are present in very low amounts in the solution, values of C (4.2 J g^{-1} $°C^{-1}$) and ρ (1 g cm^{-3}) for water were used in the calculations.

For example, the surface temperature of silkworm excrement powder was 49.4 °C during the irradiation process, and the initial temperature is 21.8 °C, therefore ΔT is 27.6 °C. As the above formulas.

$Q_1 = C\rho V\Delta T_1 = 4.2 \times 1 \times 1 \times (49.4 - 21.8) = 115.92\,J$

$Q_2 = C\rho V\Delta T_2 = 4.2 \times 1 \times 1 \times (41.7 - 20.6) = 88.62\,J$

$E = PSt = 0.1 \times 2.545 \times 1200 = 305.4\,W \cdot s$

$$\eta = \frac{Q_1 - Q_2}{E} = (115.92 - 88.62)/305.4 = 8.94\%$$

As a result, silkworm excrement energy conversion efficiency $\eta = (Q_1\text{-}Q_2)/E = 8.94\%$ when the temperature difference is 27.6 °C is calculated.

The surface temperature of the carbonized mulberry leaves powder was 47.5 °C during the irradiation process, and the initial temperature is 21.9 °C, therefore ΔT is 25.6 °C. As the above formulas.

$Q_1 = C\rho V\Delta T_1 = 4.2 \times 1 \times 1 \times (47.5 - 21.9) = 107.52\,J$

$Q_2 = C\rho V\Delta T_2 = 4.2 \times 1 \times 1 \times (39.8 - 20.2) = 82.32\,J$

$E = PSt = 0.1 \times 2.545 \times 1200 = 305.4\,W \cdot s$

$$\eta = \frac{Q_1 - Q_2}{E} = (107.52 - 82.32)/305.4 = 8.25\%$$

As a result, the carbonized mulberry leaves energy conversion efficiency $\eta = (Q_1\text{-}Q_2)/E = 8.25\%$ when the temperature difference is 25.6 °C is calculated.

The surface temperature of mulberry leaves powder was 45.7 °C during the irradiation process, and the initial temperature is 20.8 °C, therefore ΔT is 24.9 °C. As the above formulas.

$Q_1 = C\rho V\Delta T_1 = 4.2 \times 1 \times 1 \times (45.7 - 20.8) = 104.58\,J$

$Q_2 = C\rho V\Delta T_2 = 4.2 \times 1 \times 1 \times (40.5 - 19.4) = 88.62\,J$

$E = PSt = 0.1 \times 2.545 \times 1200 = 305.4\,W \cdot s$

$$\eta = \frac{Q_1 - Q_2}{E} = (104.58 - 88.62)/305.4 = 5.23\%$$

As a result, mulberry leaves energy conversion efficiency $\eta = (Q_1\text{-}Q_2)/E = 5.23\%$ when the temperature difference is 24.9 °C is calculated.

Calculation of the efficiency for solar to vapor generation: The conversion efficiency η of solar energy in photothermal assisted water evaporation was calculated as the following formula.

$$\eta = \frac{\dot{m} h_{LV}}{C_{opt} P_0}$$

Where $\dot{m}$ refers to the mass flux (evaporation rate) of water (i.e., $\dot{m} = m_{solar} - m_{dark}$), m_{solar} is the evaporation rate under solar irradiation and m_{dark} is the evaporation rate under dark circumstance, h_{LV} refers to the total liquid vapor phase-change enthalpy (i.e., the sensible heat and the enthalpy of vaporization (i.e., $h_{LV} = Q + \Delta h_{vap}$)), Q is the energy provided to heat the system from the initial temperature to a final temperature, Δh_{vap} is the latent heat of vaporization of water P_0 is the nominal solar irradiation value of 1.0 kW m^{-2}, and C_{opt} represents the optical concentration. The schematic for the vaporization enthalpy of the vapor was as follows.

$$Q = C_{liquid} \times \left(T - T_0\right)$$

$$\Delta h_{vap} = Q_1 + \Delta h_{100} + Q_2$$

$$Q_1 = C_{liquid} \times (100 - T)$$

$$Q_2 = C_{vapor} \times (T - 100)$$

In this work, C_{liquid}, the specific heat capacity of liquid water is a constant of 4.18 J (g °C)$^{-1}$. C_{vapor}, the specific heat capacity of water vaper is a constant of 1.865 J (g °C)$^{-1}$. Δh_{100} is the latent heat of vaporization of water at 100 °C, taken to be 2260 kJ kg^{-1}. The surface temperature of the silkworm excrement hydrogel was 44.6 °C during the evaporation process, therefore T is 44.6 °C. As the above formulas,

$$Q = C_{liquid} \times \left(T - T_0\right) = 4.18 \times (44.6 - 20.4) = 101.156\ kJ\ kg^{-1}$$

$$\Delta h_{vap} = Q_1 + \Delta h_{100} + Q_2 = 4.18 \times (100 - 44.6) + 2260 + 1.865 \times (44.6 - 100)$$
$$= 2388.251\ kJ\ kg^{-1}$$

$$h_{LV} = Q + \Delta h_{vap} = 101.156 + 2388.251 = 2489.407\ kJ\ kg^{-1}$$

$$m_{solar} = 1.4205\ kg\ m^{-2}\ h^{-1}$$

$$m_{dark} = 0.1674\ kg\ m^{-2}\ h^{-1}$$

$$\dot{m} = m_{solar} - m_{dark} = 1.2531\ kg\ m^{-2}\ h^{-1}$$

$$P_0 = 1000\ W\ m^{-2}$$

$C_{opt} = 1$

As a result, water evaporation rate is 1.42 kg m^{-2} h^{-1}, evaporation efficiency η = $\dot{m}h_{LV}/C_{opt}P_0$ = 86.65% when the latent heat of water vaporization at 44.6 °C (2489.407 kJ kg^{-1}) is used in calculation.

Calculation of Conduction loss η_{cond}:

The conductive heat flux from SE/H to water is calculated as follows:

$$P_{cond} = \frac{Cm\Delta T}{At} = \frac{4.18 \times 4 \times 6}{0.00049 \times 1800} = 113\ W\ m^{-2}$$

$$\eta_{cond} = \frac{P_{cond}}{P_{in}} = \frac{113}{1000} = 11.3\%$$

Where *C* is the specific heat capacity of liquid water (4.18 J g^{-1} °C), *t* is the irradiation time(1800 s), *m* is the water weights (~ 4 g) and ΔT is increased temperature of the bulk water within 30 min, *A* is the projected area (0.00049 m^2).

Calculation of Radiation loss η_{rad}:

The radiation flux is based on Stefan-Boltzmann law, which is calculated as follows：

$$P_{rad} = \varepsilon\sigma(T_2^4 - T_1^4) = 0.087 \times 5.67 \times 10^{-8} \times (301.9^4 - 295.1^4) = 36\ W\ m^{-2}$$

$$\eta_{rad} = \frac{P_{rad}}{P_{in}} = \frac{36}{1000} = 3.6\%$$

where ε (0.874) is the emissivity, σ is the Stefan-Boltzmann constant 5.67 × 10^{-8} W (m^{-2} K^4)$^{-1}$, T_2 (301.9 K) is the temperature at the surface of SE/H steam generator,and T_1 (295.1 K) is the temperature of the adjacent environment of steam generator after 1800 s irradiation. The emissivity of SE/H is 0.874, which is calculated using an absorption spectrum and plank formula.

Calculation of Convection loss η_{conv}:

The convection heat loss is calculated based on Newton's law of cooling.

$$P_{conv} = h(T_2 - T_1) = 5 \times (301.9 - 295.1) = 34\ W\ m^{-2}$$

$$\eta_{conv} = \frac{P_{conv}}{P_{in}} = \frac{34}{1000} = 3.4\%$$

Where h is the heat transfer coefficient is approximately 5 W m^{-2} K according to the previously reports. T_2 (301.9 K) is the temperature at the surface of SE/H, T_1 (295.1 K) is the temperature of the adjacent environment of steam generator.

Swelling rate: At room temperature, the dried SE/H sample was added into 50 mL of water. The sample was taken out of the water after 12 h, and the surface water was wiped with filter paper; its mass was weighed with a precision electronic balance. The following formulas were used to calculate the swelling rate (%) of the hydrogel.

$$\frac{m_t - m_0}{m_0} \times 100 = (2.2486 - 0.6578)/0.6578 = 242\ \%$$

where m_0 and m_t represent the initial dried sample weight and the weight of the swollen sample at time t, respectively.

Supplementary figures:

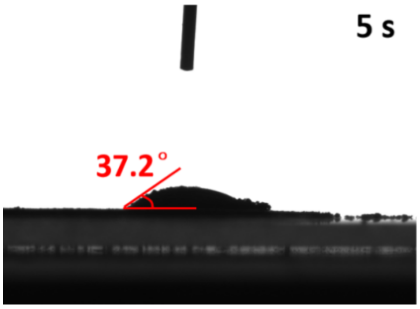

Figure S1. Digital photograph of water contact angle measurement for the surface of SE powder.

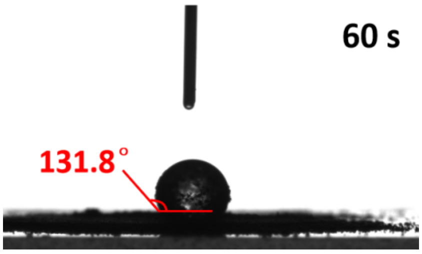

Figure S2. Digital photograph of water contact angle measurement for the surface of ML powder.

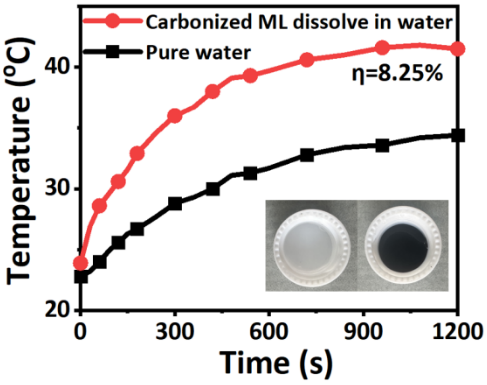

Figure S3. Photothermal behavior of pure water and carbonized ML dissolve in water under 1.0 kW m^{-2} solar irradiation for 20 minutes.

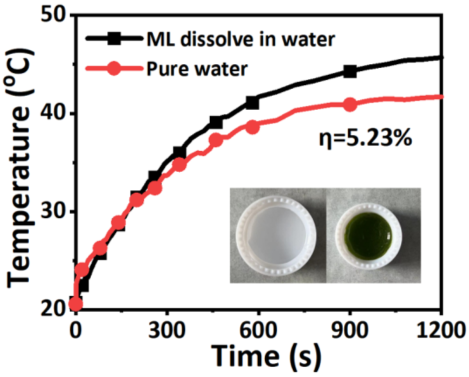

Figure S4. Photothermal behavior of pure water and ML dissolve in water under 1.0 kW m^{-2} solar irradiation for 20 minutes.

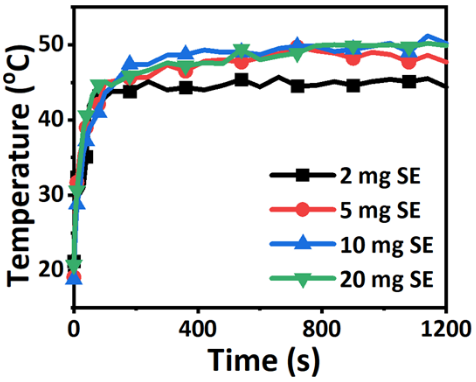

Figure S5. Temperature changes of SE powder (2 mg, 5 mg, 10 mg and 20 mg) under 1.0 kW m^{-2} irradiation for 20 minutes.

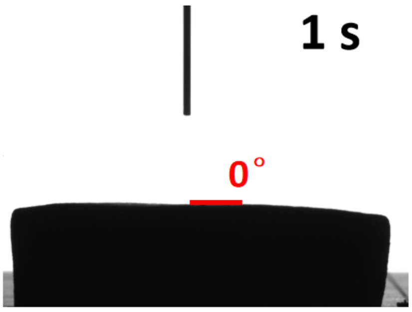

Figure S6. Digital photograph of water contact angle measurement for the surface of SE/H.

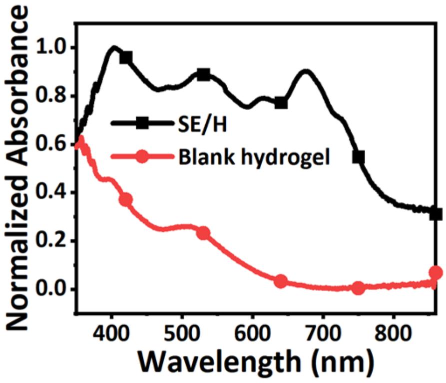

Figure S7. The light absorption spectra of SE/H and blank hydrogel.

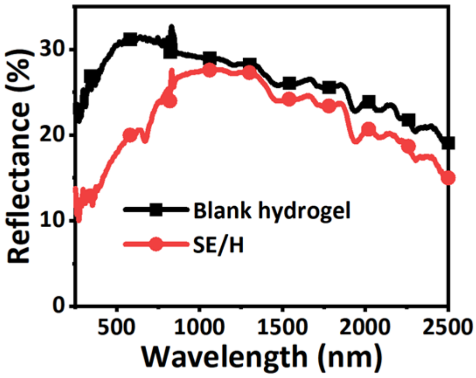

Figure S8. The light reflection spectra of SE/H and blank hydrogel.

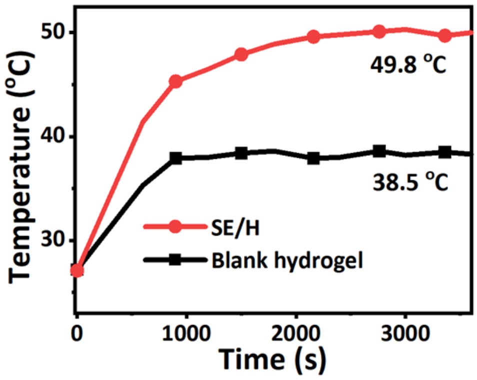

Figure S9. Photothermal behavior of blank hydrogel and SE/H under 1.0 kW m^{-2} solar irradiation.

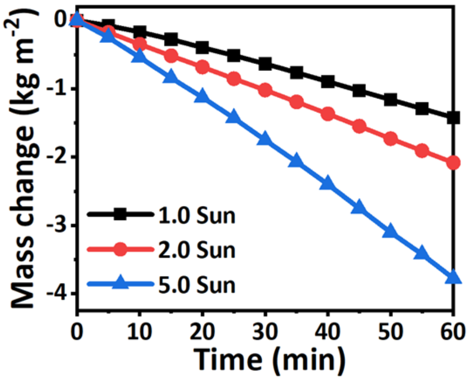

Figure S10. Water mass reduction using SE/H under the irradiation intensities of 1.0, 2.0 and 5.0 sun.

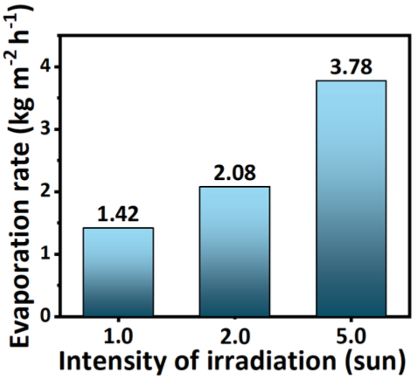

Figure S11. Evaporation rate using SE/H under 1.0, 2.0 and 5.0 irradiation intensities.

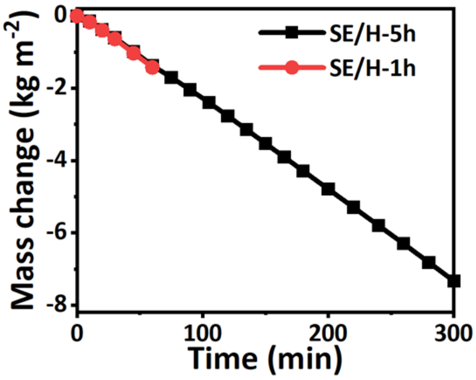

Figure S12. Mass loss curves of SE/H under simulated solar irradiation of 1.0 kW m^{-2} within 1 hour and 5 hours.

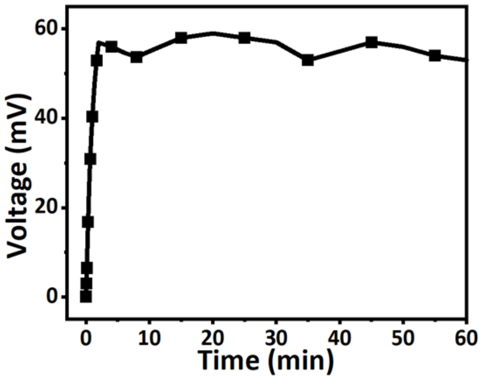

Figure S13. Corresponding output voltages of SE/H under 1.0 kW m^{-2} for 1 hour.

Table S1. The water evaporation rate and water evaporation conversion efficiency of different photothermal functional materials under 1.0 kW m^{-2} simulated solar irradiation.

System	**Materials**	**Evaporation rate (kg m^{-2} h^{-1})**	**Evaporation conversion efficiency (%)**	**Ref.**
Biomass material	SE/H	1.420	86.65	This work
	FPyPP	1.220	76.61	1
	BPC-PS-U	1.386	90.88	2
	CL+AL	1.360	83.70	3
	SCW	1.525	78.44	4
	Loofah-based Evaporator	1.420	89.90	5
	VSI-700	1.050	86.50	6
	PPy-bamboo	1.125	76.87	7
Organic material	GDPA-QCN	1.300	90.40	8
	AFQ	1.330	57.00	9
	TPA-TPA-O6	1.293	89.41	10
	PPy@D-SCG	1.540	89.10	11
	GT-COF-3	1.314	90.70	12
Inorganic material	TA/Fe^{3+}-bamnoo	1.152	78.86	13
	Mxene/CNTs	1.350	88.20	14
	Carbon fiber	1.300	80.00	15

	PCMs-PTC	1.267	90.00	16
	Ti_3C_2-MnO_2@LS	1.360	85.28	17

1. C. Zhang, P. Xiao, F. Ni, L. Yan, Q. Liu, D. Zhang, J. Gu, W. Wang and T. Chen, *ACS Sustainable Chem. Eng.,* 2020, **8**, 5328.

2. H. M. Wilson, D. J. Ahirrao, S. R. Ar and N. Jha, *Sol. Energy Mater. Sol. Cells*, 2020, **215**, 110604.

3. Y. Lu, X. Wang, D. Fan, H. Yang, H. Xu, H. Min and X. Yang, *Sustainable Mater. Technol.*, 2020, **25**, e00180.

4. H. Hu, Y. Feng, X. Chen, L. Tian, Z. Yin, H. Wang, Y. Li, Y. Yang and Q. Sun, *J. Environ. Chem. Eng.*, 2024, **12**, 113419.

5. C. Liu, K. Hong, X. Sun, A. Natan, P. Luan, Y. Yang and H. Zhu, *J. Mater. Chem. A,* 2020, **8**, 12323.

6. W. Zhang, X. Chen, G. Zhang, J. Li, Q. Ji, C. Hu, Z. J. Ren, H. Liu and J. Qu, *J. Mater. Chem. A,* 2020, **8**, 12089.

7. P. Zhang, M. Xie, Y. Jin, C. Jin and Z. Wang, *ACS Appl. Polym. Mater.*, 2022, **4**, 2393.

8. J. Liu, Y. Cui, Y. Pan, Z. Chen, T. Jia, C. Li and Y. Wang, *Angew. Chem. Int. Ed.*, 2022, **61**, e202117087.

9. Y.-T. Chen, X. Wen, J. He, Z. Li, S. Zhu, W. Chen, J. Yu, Y. Guo, S. Ni, S. Chen, L. Dang and M. D. Li, *ACS Appl. Mater. Interfaces*, 2022, **14**, 28781.

10. Z. Wang, J. Zhou, Y. Zhang, W. Zhu and Y. Li, *Angew. Chem. Int. Ed.*, 2022, **61**, e202113653.

11. C. Shi, X. Zhang, A. Nilghaz, Z. Wu, T. Wang, B. Zhu, G. Tang, B. Su and J. Tian, *Chem. Eng. J.*, 2023, **455**, 14036.

12. Y. Y. Li, T. Wei, C. Liu, Z. Zhang, L. F. Wu, M. Ding, S. Yuan, J. Zhu and J. L. Zuo, *Chem-Eur J*, 2023, **29**, e202301048.

13. P. Zhang, X. Piao, H. Guo, Y. Xiong, Y. Cao, Y. Yan, Z. Wang and C. Jin, *Ind Crop Prod*, 2023, **200**, 116823.

14. Y. Wang, Q. Qi, J. Fan, W. Wang and D. Yu, *Sep. Purif. Technol.*, 2021, **254**,

117615.

15. W. Zhao, H. Gong, Y. Song, B. Li, N. Xu, X. Min, G. Liu, B. Zhu, L. Zhou, X. X. Zhang and J. Zhu, *Adv. Funct. Mater.*, 2021, **31**, 2100025.

16. L. Wang, G. Liu, S. Li and Y. Shi, *Chem. Eng. J.*, 2025, 161599.

17. A. M. Saleque, S. Ma, A. K. Thakur, R. Saidur, T. K. Han, M. I. Hossain, W. Qarony, Y. Ma, R. Sathyamurthy and Y. H. Tsang, *Desalination*, 2023, **554**, 116488.