Composite polymer hydrogels as draw agents in forward osmosis and solar dewatering

Dan Li,[a] Xinyi Zhang,[a] Jianfeng Yao,[a] Yao Zeng,[a] George P. Simonb[b] and Huanting Wang*[a]

Supplementary Information

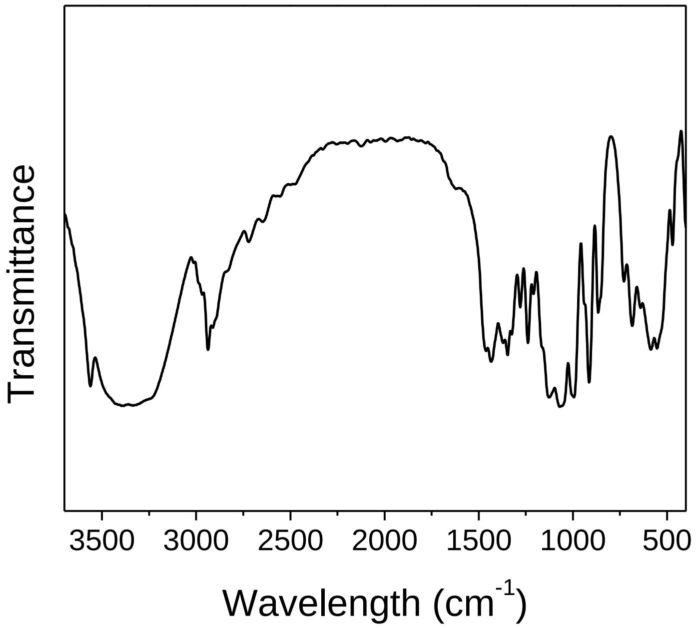

Fig. S1. FT-IR spectrum of sucrose before the hydrothermal carbonization.

Preparation of C-S carbon spheres

The solution, in which 2 g of sucrose was completely dissolved in 5 g of deionized (DI) water, was sealed into a Teflon stainless autoclave and hydrothermally reacted in a pre-heated oven at 190 °C for 2.4 h. After the reaction, the autoclave was cooled down in a water bath to room temperature. The obtained black solid powders were then separated and filtered by using filter papers, which were repeatedly washed by DI water and then dried at 70 °C under vacuum. These fabricated carbon particles were denoted to C-S.

Fig. S2 shows the SEM image of C-S sample with controllable monodispersed particle sizes, ranging from 2 to 5 μm.

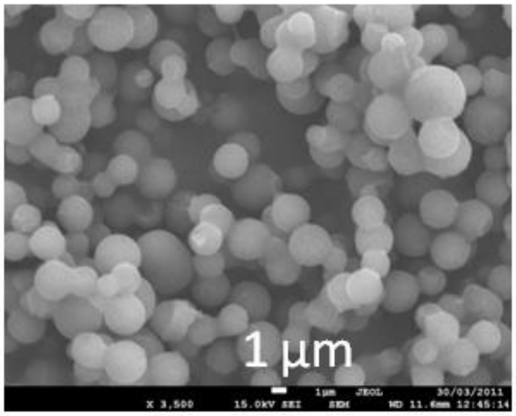

Fig. S2. SEM image of C-S carbon particles.

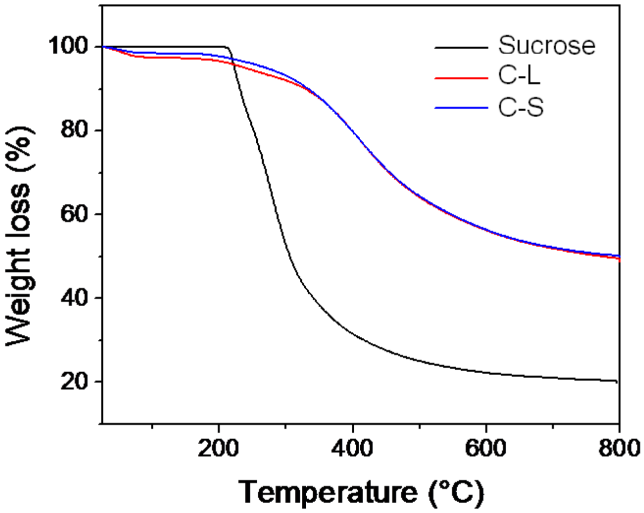

Fig. S3. TGA results of sucrose and carbon samples. Thermogravimetric analysis (TGA, Perkin Elmer, Pyris 1 analyzer) was performed at a heating rate of 5 °C/min from 25 °C to 800 °C in N_2 with a flow rate of 20 cm^3 min^{-1}.

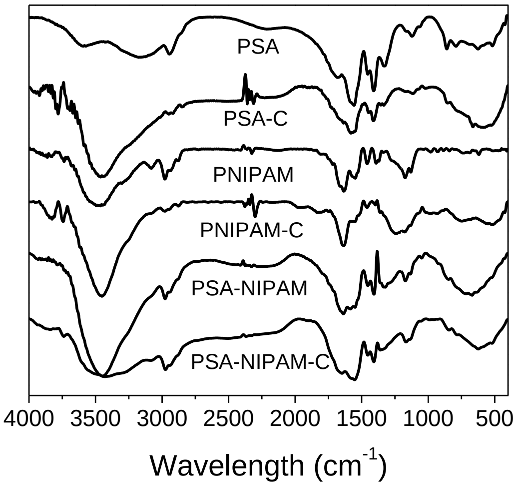

Fig. S4. FT-IR spectra of pure (e.g. PSA, PNIPAM and PSA-NIPAM) and composite (e.g. PSA-C, PNIPAM-C and PSA-NIPAM-C) polymer hydrogels with the incorporation of C-L carbon particles.

Fig. S4 shows the FT-IR spectra of different pure polymer hydrogels, including PSA, PNIPAM, and PSA-NIPAM; and the corresponding composite polymer hydrogels with the addition of carbon particles (PSA-C, PNIPAM-C and PSA-NIPAM-C). In the spectra of PSA and corresponding PSA-C, the absorbance 2940 cm^{-1} and 1455 cm^{-1} are attributed to the –CH_2 stretching and bending vibration. Two strong absorption peaks are observed at around 1570 cm^{-1} and 1410 cm^{-1}, assigned to the C=O stretching vibration of the ionized carboxyl group (–COO−).[28] In the FTIR spectra of PNIPAM and PNIPAM-C, the main peak assignments are as follows: 3292 cm^{-1} (secondary amide N–H stretching), 2970 cm^{-1} (–CH_3 asymmetric stretching), 1650 cm^{-1} (secondary amide C=O stretching, aka amide I bond), and 1550 cm^{-1} (secondary amide C=O stretching, aka amide II bond).[29] Similar characteristic peaks in PSA or PNIPAM polymer hydrogels can also be observed in the spectra of PSA-NIPAM and PSA-NIPAM-C samples, confirming the presence of NIPAM and SA units in the copolymer hydrogels. However, there are no significant characteristic peaks of the hydrophilic carbon particles observed in the FTIR spectra of composite polymer hydrogels, which may be ascribed to the presence or obscuring of strong transmittance peaks arising from polymer structures.

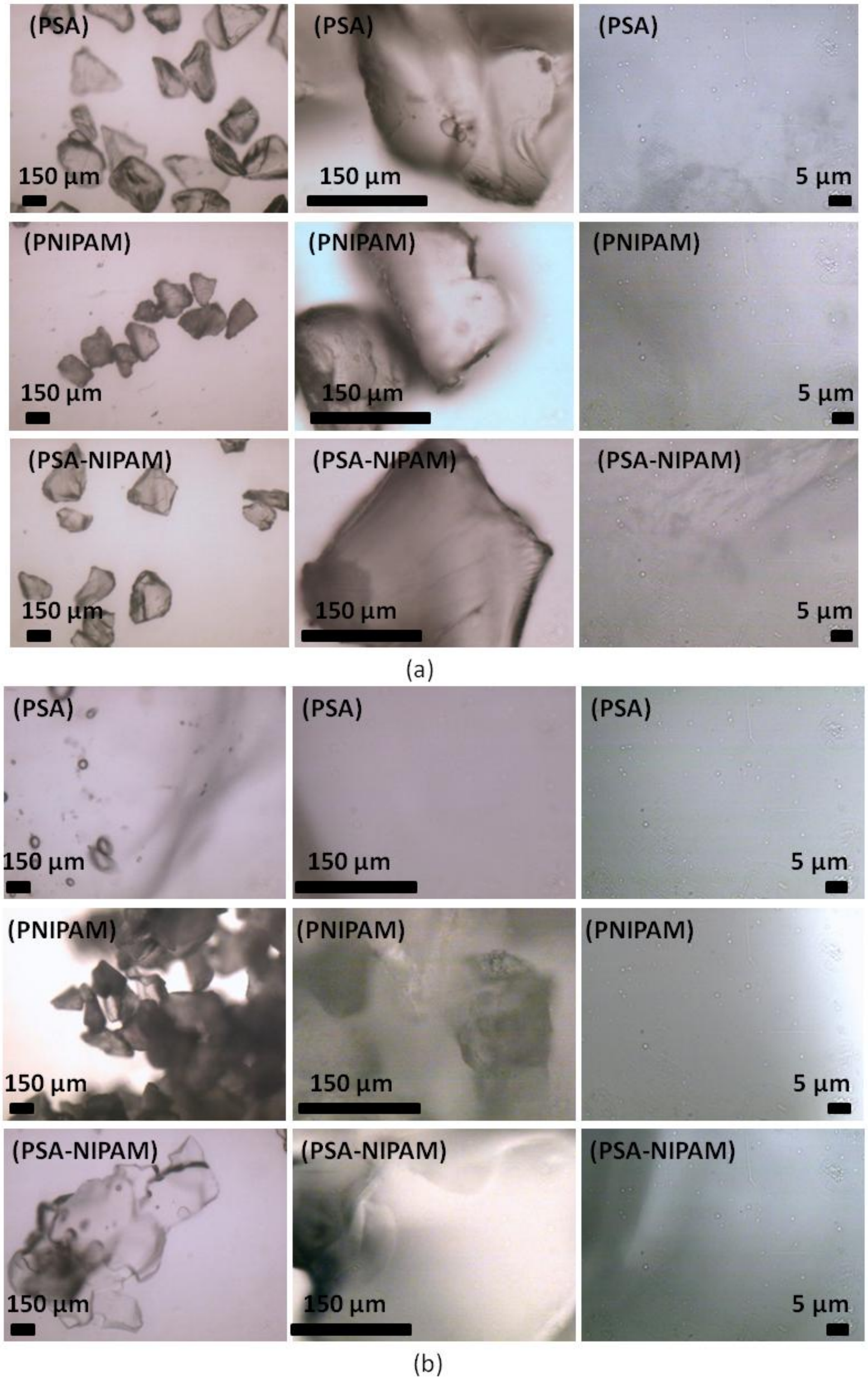

Fig. S5. Optical microscopy images at different magnifications of pure polymer hydrogels: (a) dry-state before 24 h FO process; and (b) wet-state after 24 h FO process.

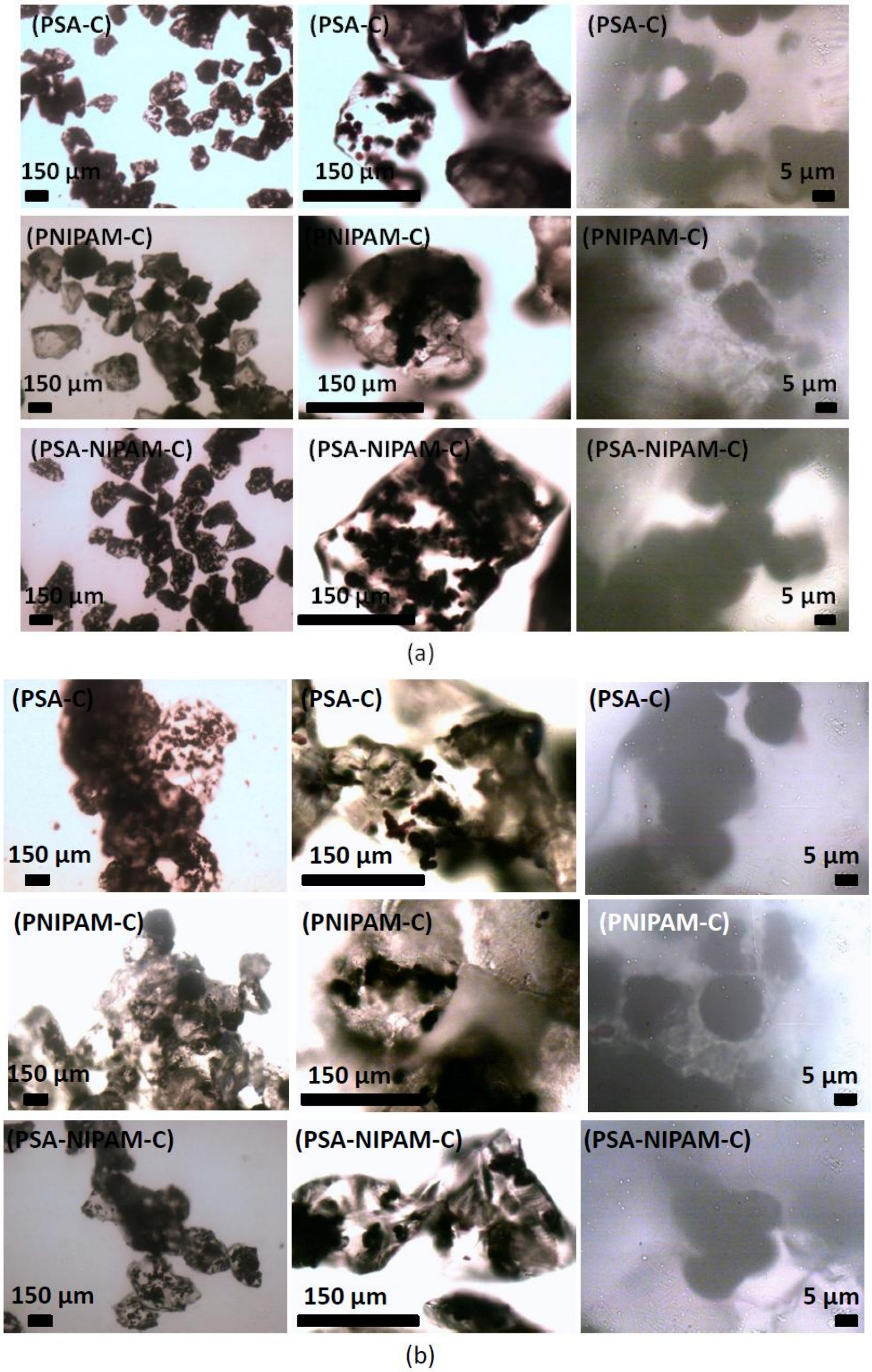

Fig. S6. Optical microscopy images of composite polymer hydrogels with 1:1 molar ratio of monomers and C-L carbon particles at different magnifications: (a) dry-state before 24 h FO process; and (b) wet-state after 24 h FO process.

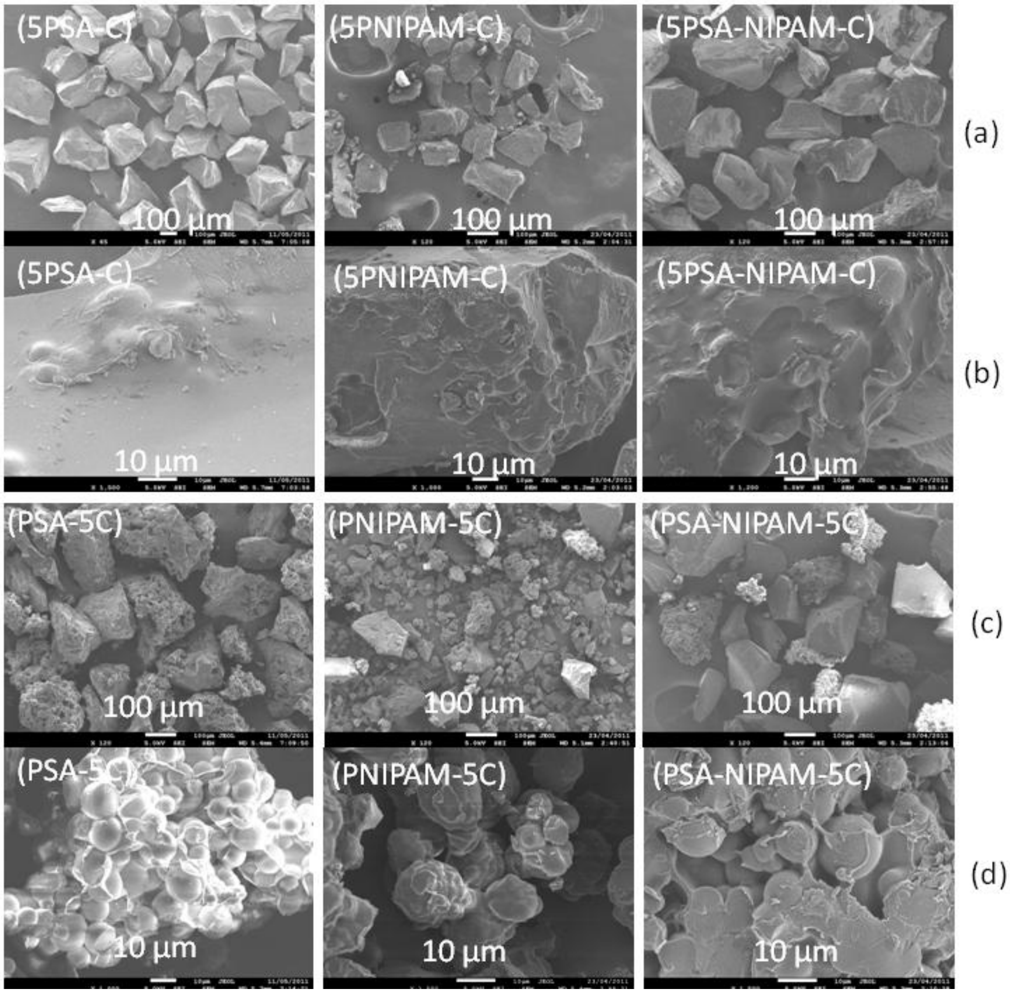

Fig. S7. SEM images of fabricated composite polymer hydrogels at low magnification (a and c) and high magnification (b and d): (a) and (b) composite polymer hydrogels with 5:1 molar ratio of monomers and C-L carbon; (c) and (d) composite polymer hydrogels with 1:5 molar ratio of monomers and C-L carbon.

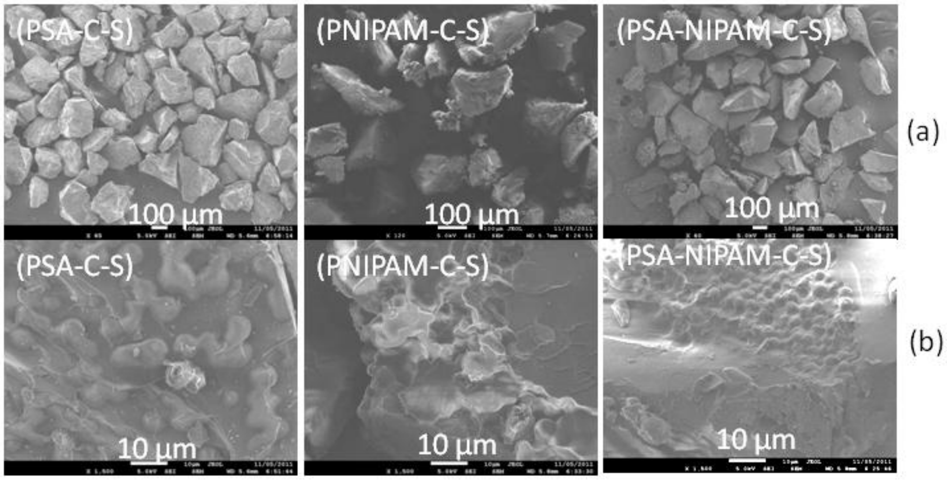

Fig. S8. SEM images of composite polymer hydrogels composed of equal moles of C-S carbon spheres (2 − 5 µm in size) and monomers at low magnification (a) and high magnification (b).

Determination of the ratio of liquid/vapor water, and the purity of water produced in the dewatering process

The percentage of liquid water in the total water loss during the dewatering was determined as follows.

The dewatering experiments were conducted with the exposure of swollen composite polymer hydrogels composed of equal moles of C-L carbon particles and monomers (water content of 66.7%) to the sunlight (1.0 kW/m^2) up to 1 h. Polymer hydrogels were placed on the wiper (Kimwipes), which was changed every 10 min. At the same time, a wiper was gently placed onto the top surface of polymer hydrogel to absorb the water released from the gel surface. The wipers were weighed for the calculation of recovered liquid water. After 1 h dewatering, the composite polymer hydrogels were weighed and compared with the initial weight of swollen polymer hydrogels to calculate the total weight loss of water.

The results are shown in Fig. S9. After the exposure of PNIPAM-C to the sunlight with an irradiation intensity of 1.0 kW/m^2 for 10 min, around 50% of water loss is liquid water. In other words, 54% of water is evaporated during dewatering. After the extended exposure of hydrogels to sunlight, the amount of liquid water, that can be recovered from the swollen PNIPAM-C, decreases. This can be explained by the faster evaporation of water at higher temperatures inside the polymer hydrogels (see Fig. 6). Only up to 9% of water loss in PSA-C is liquid water, due to the strong interaction between polymer hydrogels and water molecules. However, the increasing temperature of hydrogels, induced by solar heating, leads to the evaporation of water inside the swollen PSA-C. PSA-NIPAM-C exhibits a slightly higher recovery rate of liquid water (12%) as compared to PSA-C.

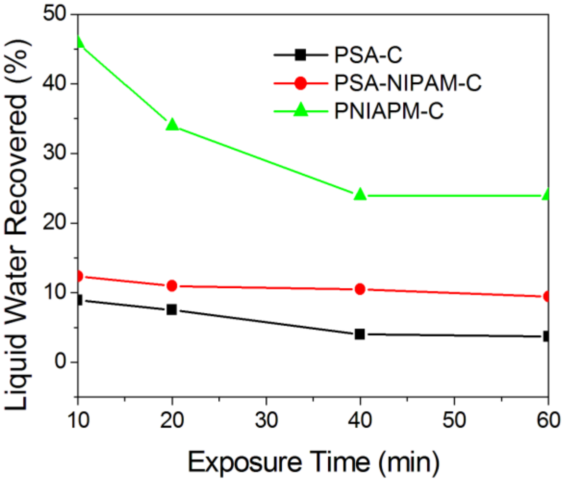

Fig. S9. Percentage of liquid water in the total amount of water recovered from swollen composite hydrogels with the equal molar ratio of carbon particles and monomers. The test was conducted with the exposure of hydrogels to the sunlight with the irradiation intensity of 1.0 kW/m^2.

The purity of water recovered was determined as follows: In FO process, 1 g of composite polymer hydrogels was used as the draw agent. After 24 h FO process, the swollen composite polymer hydrogels were taken out from the setup and completely dried in the oven. The dry powders were immersed into 1 L water overnight. The solution with swollen polymer hydrogels was then filtered to recover the water for conductivity analysis by using a conductivity meter (InoLab 730, WTW). For comparison, 1 g of fresh dry composite polymer hydrogels was treated similarly and the water conductivity was measured. By comparing the difference of conductivities, the changed conductivity can be used for the calculation of salt rejection.

$$R = 1 - \frac{C_{FO}}{C_{2000}} \times 100\%$$

where R is salt rejection; C_{FO} is the effective conductivity of the water recovered from the polymer hydrogels, and C_{2000} is the conductivity of feed solution in FO process (2000 ppm NaCl).

The FO membrane used in this work was supplied by Hydration Technologies Inc. (Albany, OR). It has a salt rejection of around 93-95%. The salt rejection during the FO process is governed by the property of FO membrane. The purity of extracted water from swollen polymer hydrogels contains 92 ppm NaCl, and the salt rejection of the FO membrane was determined to be 95.4%, which is similar to the specification from the Hydration Technologies Inc.

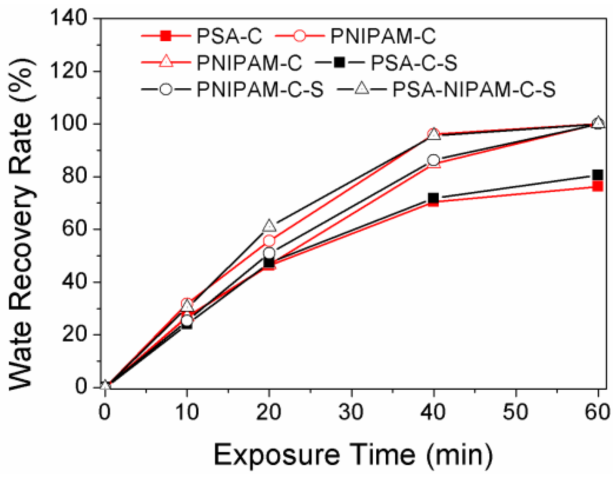

Fig. S10. Water recovery rates of swollen composite hydrogels (equal moles of carbon and monomers) with different sizes of carbon fillers, C-S and C-L, after exposure to the sunlight with an intensity of 1.0 kW/m^2.

Recycle experiments

After each FO process, the polymer hydrogels were taken out from the FO setup, and dried under exposure to the light irradiation (1.0 kW/m^2). The completely dried polymer hydrogels were re-used for the next cycle of FO test. Water fluxes were measured after 24 h FO process.

As shown in Fig. S11, the fluxes decrease by 5% after 3rd cycle of FO process, indicating that the polymer hydrogel particles show very good recycleability.

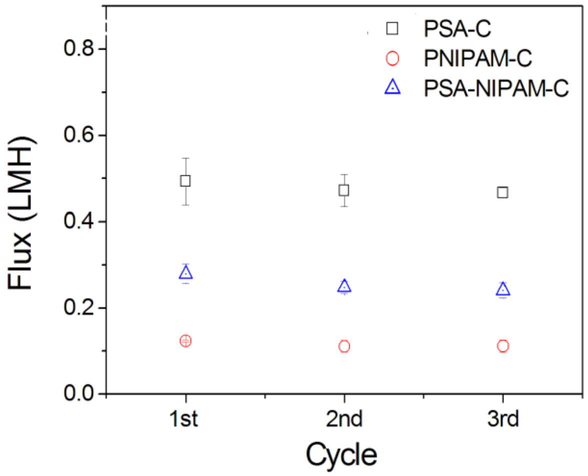

Fig. S11. Water fluxes in 24 h forward osmosis process produced by the fresh (1st cycle) and recycled (2nd and 3rd) composite polymer hydrogels.