

Supporting Information

A General Method for Selectively Coating Photothermal Materials on 3D Porous Substrate Surfaces towards Cost-Effective and Highly Efficient Solar Steam Generation

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Experimental Section

Chemicals: The Calcium Chloride (>98%), Sodium Alginate, Dopamine Hydrochloride, Thiourea (>99%) and D-glucose (>99.5%) were purchased from Sigma Pty Ltd. The Sodium Hydroxide (AR), Copper Sulfate Pentahydrate (AR), Hydrogen Peroxide (30% w/w) and Ethanol (100%) were supplied by Chem-Supply. All chemicals were used as received without further treatment. The reduced Graphene Oxide was supplied by Huasheng Corp. and well sonicated before use. Unless otherwise noted, Milli-Q water with a resistance >18.2 MΩ cm⁻¹ was used for all experiments.

Synthesis of CuO flower-like particles: The first step in synthesis of CuO particles is the preparation of Cu₂O particle precursor. Briefly, 1.25 g of Cu₂SO₄·5H₂O was dissolved into 50 mL Milli-Q water and heated to 55 °C with constant stirring at 500 rpm. The transparent blue Cu²⁺ solution was kept at 55 °C for another 2 mins before adding 30 mL NaOH solution (3 M) to form blue Cu(OH)₂. The mixture was then quickly heated to 70 °C and the blue Cu(OH)₂ turned to be dark precipitation. 5 minutes later, 0.3 g glucose was added into the suspension. The resulting mixture was maintained at 70 °C for about 20 min until a brick red precipitation gradually generated, indicating the formation of Cu₂O. The obtained red product was washed with water and ethanol several times.

Thereafter to generate CuO flower-like particles, 0.72 g of the as-prepared Cu₂O particles were dispersed into 20 mL of NaOH solution (0.1 M) by ultra-sonication. The resulting suspension was then purged with air and kept stirring for 24 h. The obtained black product was washed with water and ethanol several times.

Synthesis of CuS: The CuS nanocages were synthesized by the sulphuration of the as-prepared Cu₂O particles. Briefly, 0.32 g of the obtained Cu₂O particles were redispersed into 200 mL Milli-Q water and reacted with thiourea (0.26 g) at 90 °C for 4 hours to generate CuS nanocages. The obtained CuS nanocages were centrifuged and washed with water and ethanol several times.

Synthesis of PDA: To form PDA particles, dopamine hydrochloride (2 mg mL⁻¹) were dissolved into a Tris buffer solution (pH = 8.5, 50 × 10⁻³ M) with CuSO₄ (5 × 10⁻³ M) and H₂O₂ (19.6 × 10⁻³ M) for 1 h, followed by centrifugation and wash with water for several times.

Dip-coating of 3D porous substrates: Commercial melamine and cellulose sponges, as well as cotton were used as substrates. The two kinds of sponges were cut into a 2×2×1 cm cuboid, while the cotton was simply rolled into a 3 cm diameter rod. Before dip-coating, the sponges and cotton rod were immersed in a calcium chloride solution (0.25 wt%) for 30 s. Then, the sponges and cotton rod with pre-absorbed Ca²⁺ were immersed in 10 mL of rGO (1 mg/mL)-SA (5 mg/mL) solution for 2 min. Thereafter, the obtained samples were pre-frozen at -22 °C for 6 hours and then freeze-dried at -60 °C for 24 h. For normal dip-coating, the sponges and cotton rod were directly immersed in the rGO-SA solution.

Drop-casting of 3D porous substrates: Initially, the melamine sponge was immersed into calcium chloride solutions of different concentrations (0 wt%, 0.05 wt%, 0.1 wt%, 0.15 wt%, 0.2 wt%, 0.25 wt%) for 30 s. PTM-SA solutions were prepared by dispersing either 1) rGO nanosheets (5 mg), 2) CuO flower-like particles (50 mg), 3) CuS nanocages (50 mg) or 4) PDA nanoparticles

(30 mg) in 10 mL of SA (5 mg/mL) solution. Thereafter, 1 mL of PTM-SA solution was evenly dropped onto the surface of the sponge containing pre-absorbed Ca²⁺. The obtained samples were pre-frozen at -22 °C for 6 hours, and then freeze-dried at -60 °C for 24 h.

Characterization: Field emission scanning electron microscopy (SEM) images were recorded by a Zeiss Merlin SEM. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 2100F transmission electron microscope. UV-2600 Spectrophotometer (Shimadzu) was used to record the UV-Vis spectra of the samples. An IR camera (FLIRE64501) was used to obtain the infrared photographs.

Water Evaporation Tests: Milli-Q water and seawater were held in a 200 mL plastic bottle. A PS foam with a hole (2.5 cm × 2.5 cm) was used as a bottle cap of the bottle to hold the cotton rod which acted as a 1D water path. The photothermal evaporator was placed on the top of the cotton rod. The other end of the cotton rod was immersed in the bulk water so that the water could be continuously transferred to the photothermal evaporator by capillary action. Simulated sunlight was provided by a Newport Oriel Solar Simulator (Newport Oriel Xenon Lamp, 66485-300XF-R1). The plastic bottle was placed on an electronic balance connected to a computer, so that water mass loss could be monitored in real-time.

Energy efficiency calculation: The energy conversion efficiency for solar steam generation is calculated by the following equations:

$$\eta = \frac{m(H_{LV} + Q)}{E_{in}} \quad (1)$$

$$Q = c(T - T_1) \text{ J kg}^{-1} \quad (2)$$

$$H_{LV(T)} = 1.91846 \times 10^6 [T/(T - 33.91)]^2 \text{ J kg}^{-1} \quad (3)$$

Where m is the water evaporation rate (with dark evaporation over the samples subtracted, 0.29 kg m⁻² h⁻¹), T is the temperature of evaporation, T_1 is the initial temperature of the water, c is the

specific heat of water which is 4.2 J gK^{-1} , Q is the sensible heat of water, H_{LV} is the enthalpy that is required for vaporization of water, and E_{in} ($\text{kJ m}^{-2} \text{ h}^{-1}$) is the energy input of the incident light. The results showed that the energy conversion efficiency for the solar steam generation of the RS-0.20 was 94.9% under 1.0 sun irradiation.

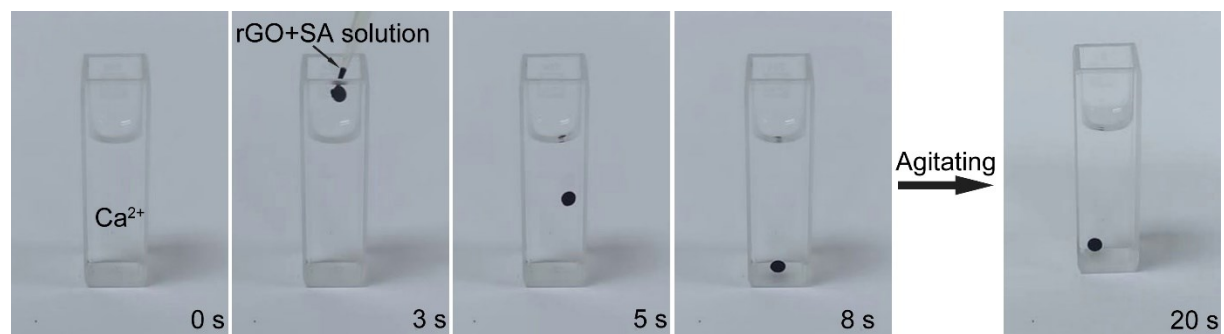


Fig. S1 Photograph illustrating the fast gelation of an rGO-SA aqueous droplet in CaCl_2 solution (0.25 wt%). The rGO-SA droplet gelled immediately in the CaCl_2 solution and preserved the shape of the droplet even after agitation.

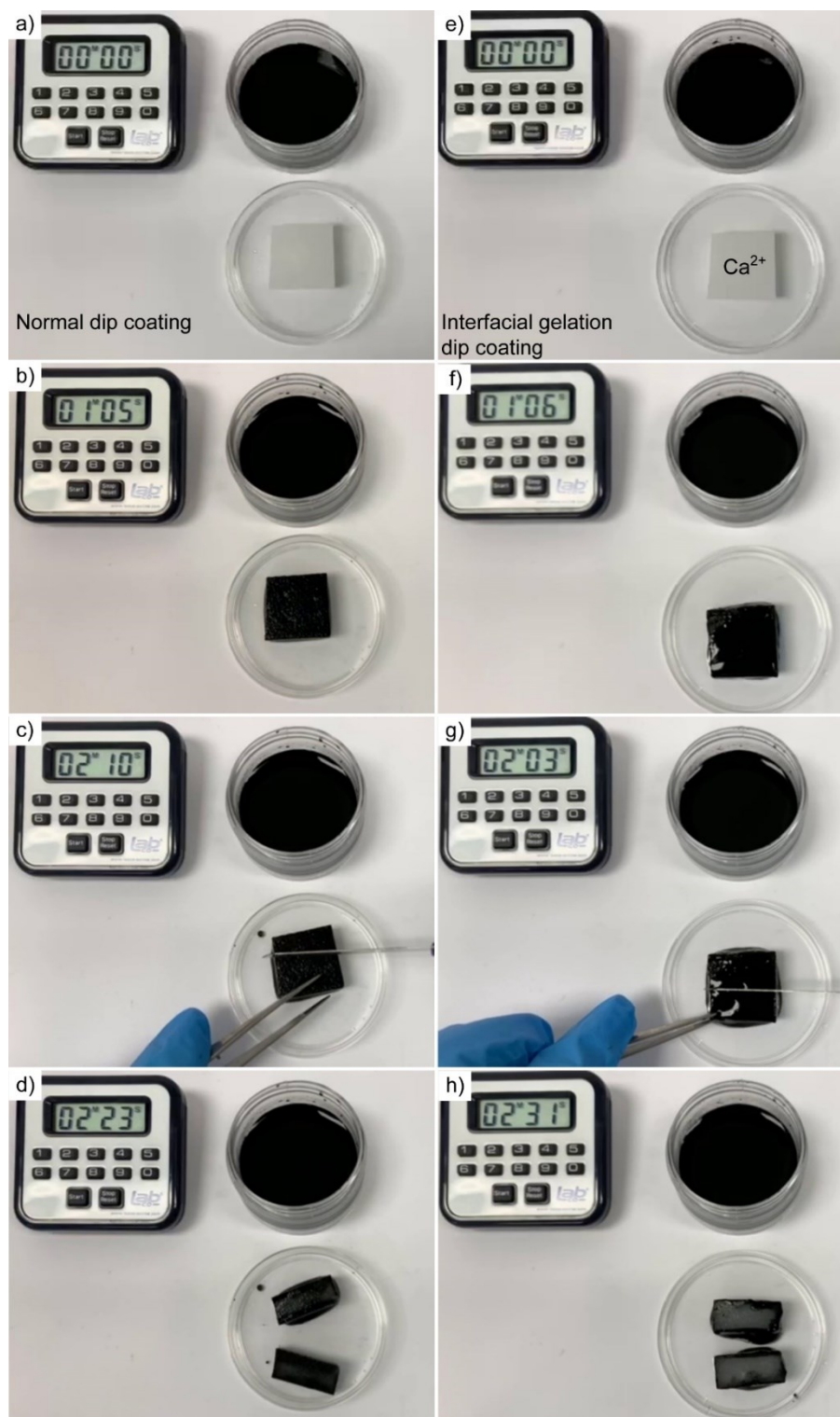


Fig. S2 Photograph illustrating (a-d) normal dip-coating and (e-f) interfacial gelation dip-coating. The normal dip-coating method resulted in even distribution of the rGO throughout the porous structure of the sponge, while the interfacial gelation dip-coating led to the selective deposition of the rGO on the surface of the porous sponge.

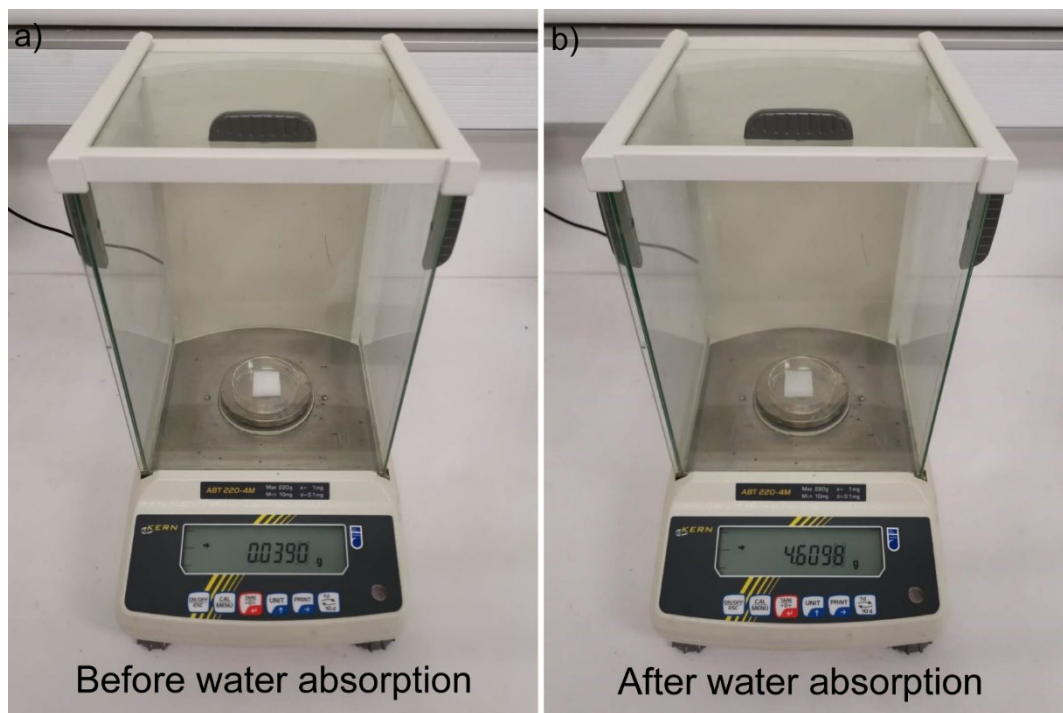


Fig. S3 Digital photographs showing the melamine sponge's ability to absorb water. a) the weight of dry sponge is 0.0390 g and b) the weight of sponge with absorbed water is 4.6098 g.

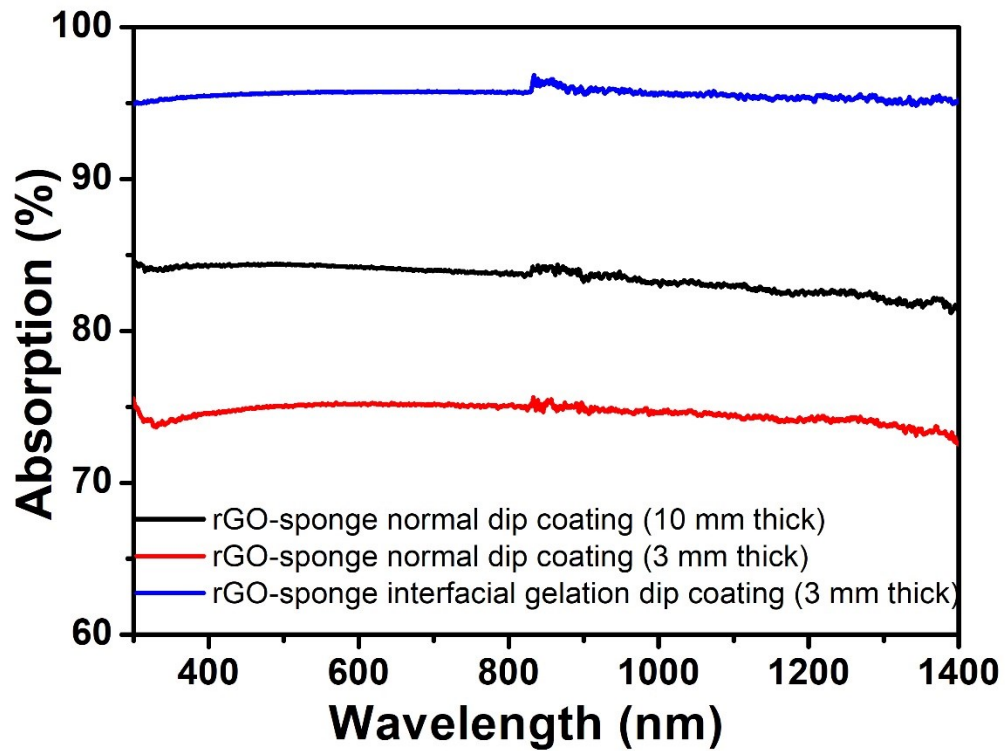


Fig. S4 Light absorption of the rGO-coated sponge fabricated by normal dip-coating and interfacial gelation dip coating methods.

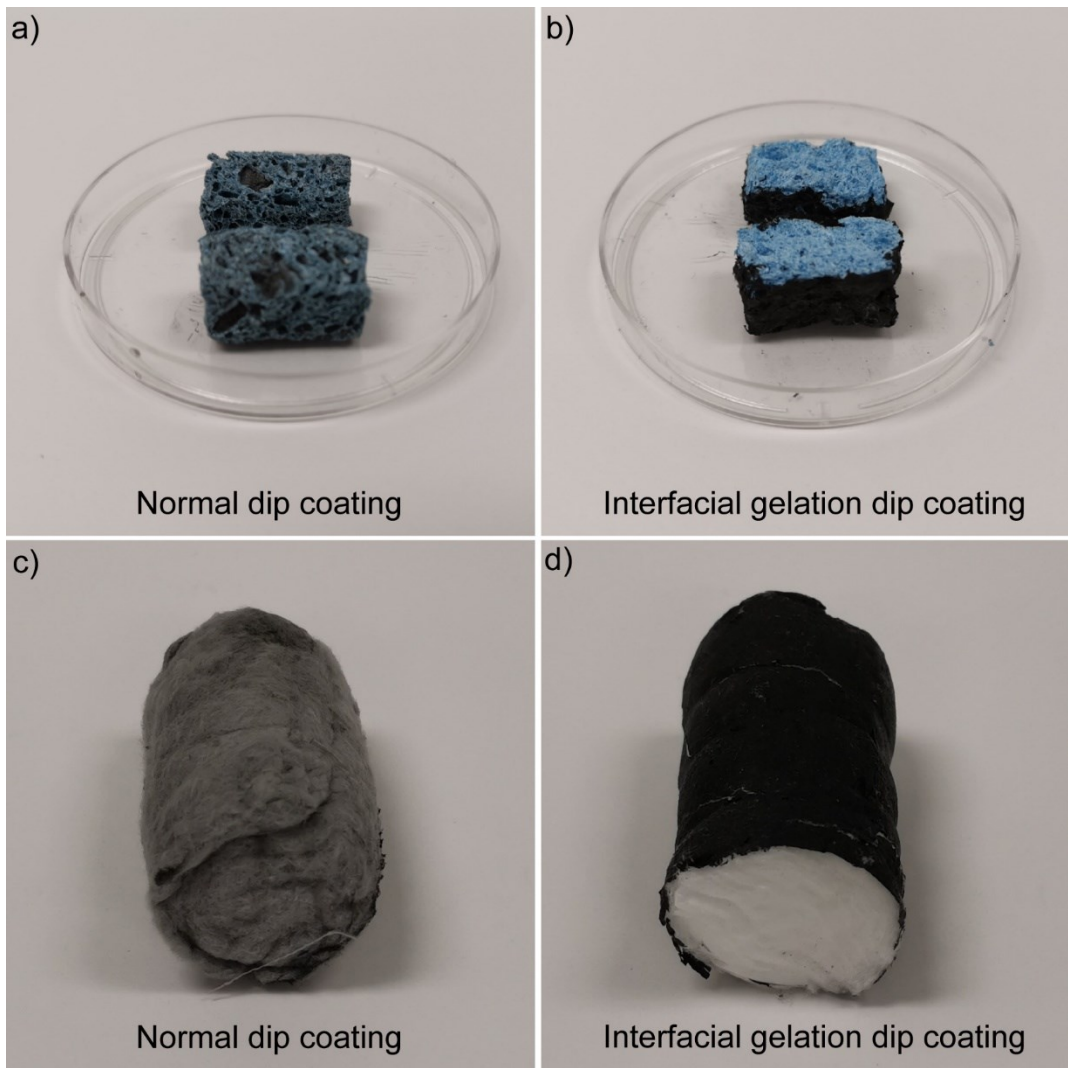


Fig. S5 Photographs of freeze-dried rGO coated cellulose sponges via normal dip-coating (a) and interfacial gelation dip-coating (b). Photographs of the rGO coated cotton rods via normal dip-coating (c) and interfacial gelation dip-coating (d).

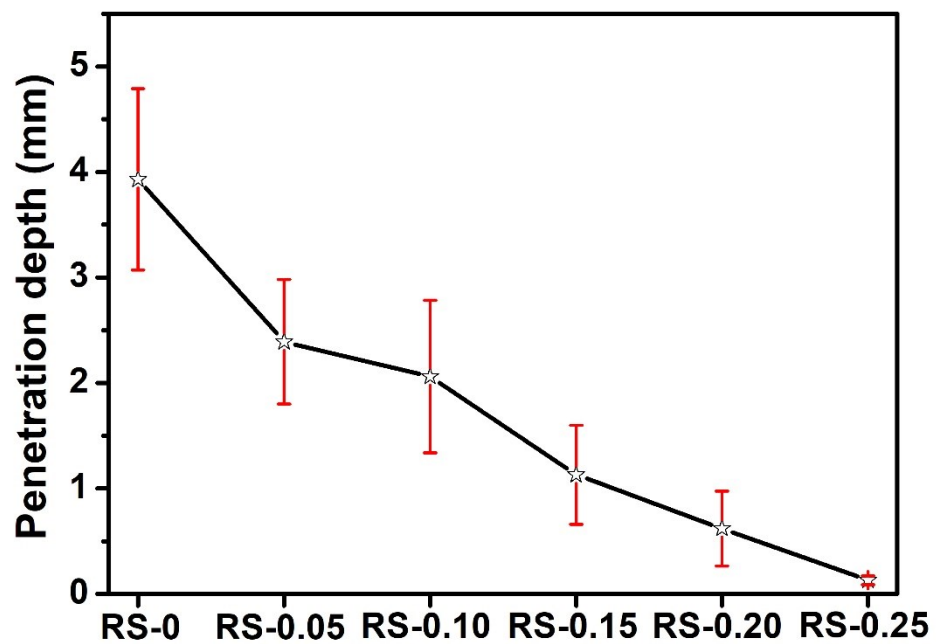


Fig. S6 Penetration depths of the rGO in the rGO-SA coated sponges (RS).

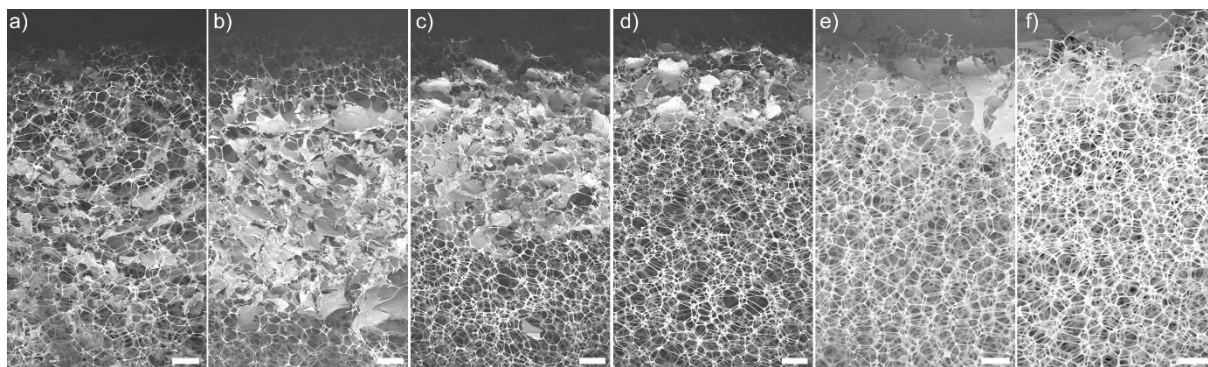


Fig. S7 SEM images of the cross-section of (a) CuSS-0, (b) CuSS-0.05, (c) CuSS-0.10, (d) CuSS-0.15, (e) CuSS-0.20, and (f) CuSS-0.25 prepared by the interfacial gelation drop-casting. Scale bar: 200 μm .

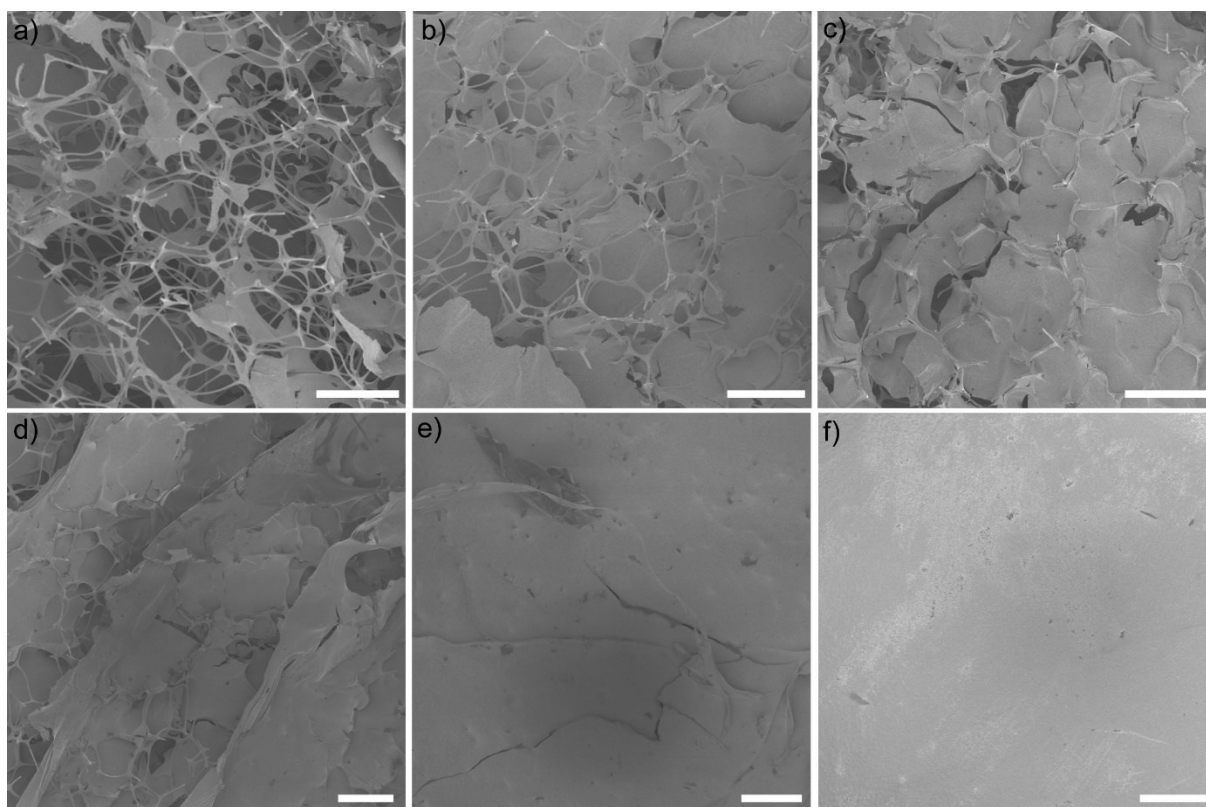


Fig. S8 SEM images of the top surfaces of (a) CuSS-0, (b) CuSS-0.05, (c) CuSS-0.10, (d) CuSS-0.15, (e) CuSS-0.20, and (f) CuSS-0.25 prepared by the interfacial gelation drop-casting. Scale bar: 200 μm .

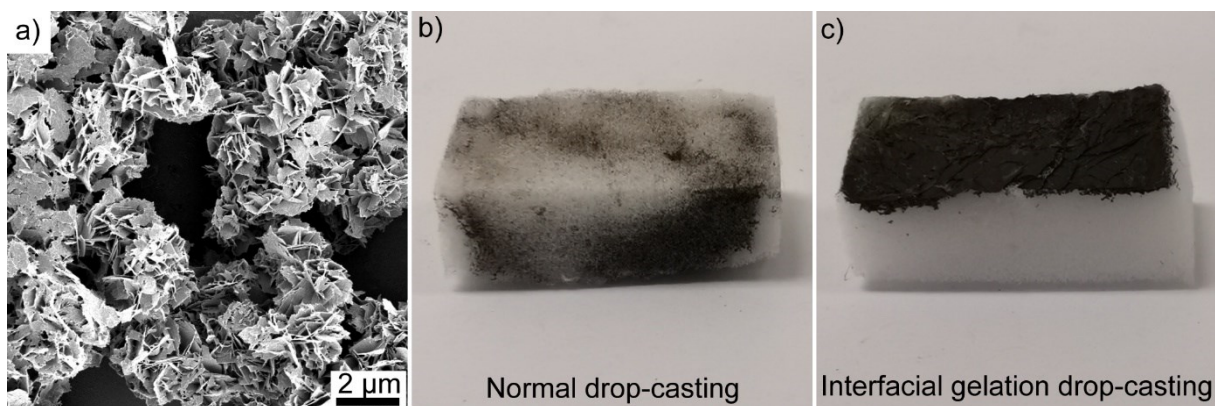


Fig. S9 (a) SEM image of CuO flower-like particles. (b, c) Digital photographs of the cross-section of the CuO coated sponge by normal drop-casting (b) and interfacial gelation drop-casting (c) methods. The concentration of the pre-absorbed Ca^{2+} is 0.25 wt% for interfacial gelation drop-casting.

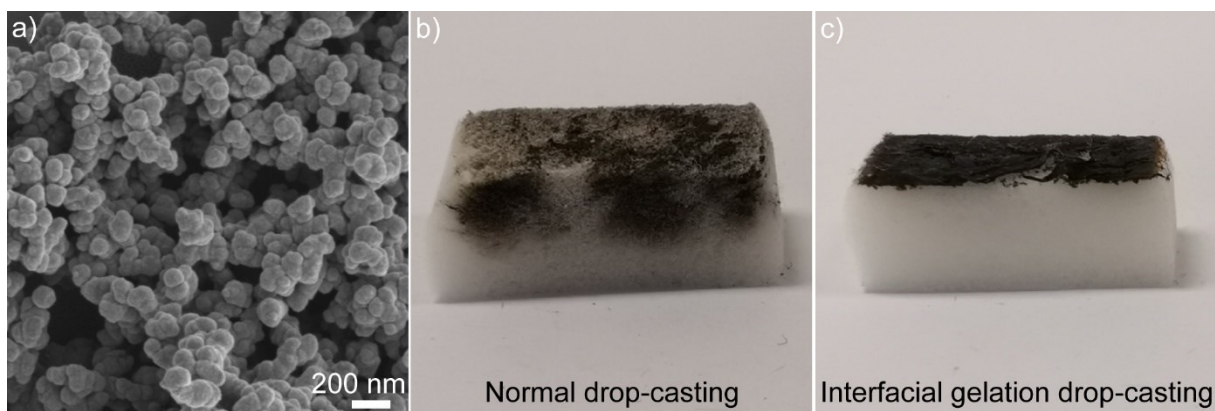


Fig. S10 (a) SEM image of PDA nanoparticles. (b, c) Digital photographs of the cross-section of the PDA coated sponge by normal drop-casting (b) and interfacial gelation drop-casting (c) methods. The concentration of the pre-absorbed Ca^{2+} is 0.25 wt% for the interfacial gelation drop-casting.

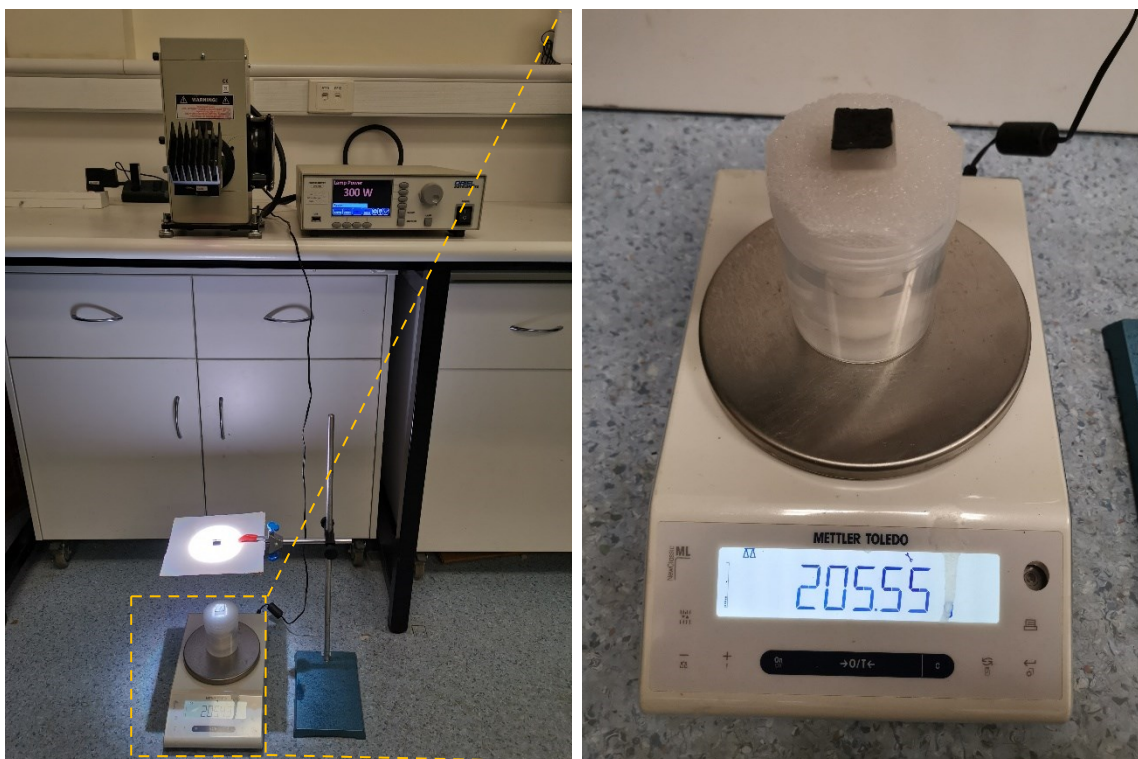


Fig. S11 Digital photographs of the oil-lamp like evaporator and setup used for the solar evaporation test.

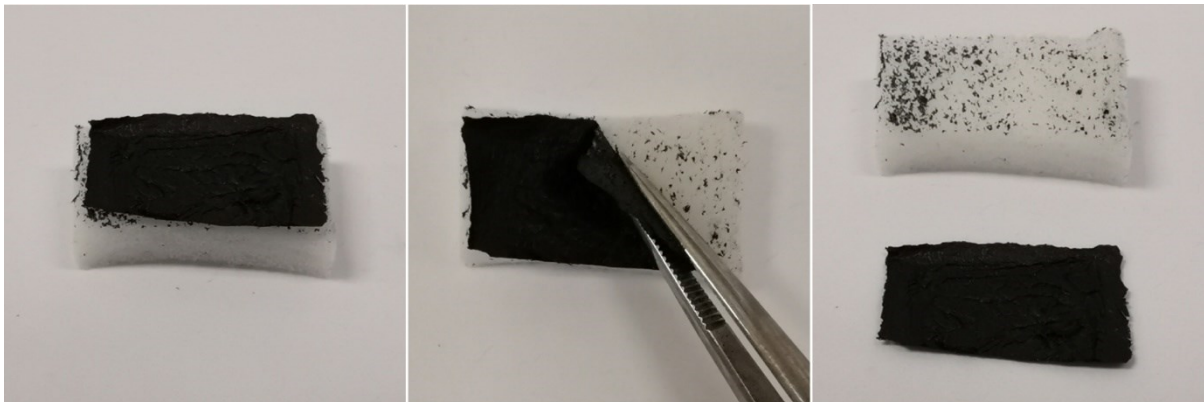


Fig. S12 Photographic illustration of the easy peeling of the rGO coating from RS-0.25 prepared by interfacial gelation drop-casting, confirming the weak connection between the rGO layer and the sponge surface due to the small rGO penetration depth. The concentration of the pre-absorbed Ca^{2+} was 0.25 wt%.

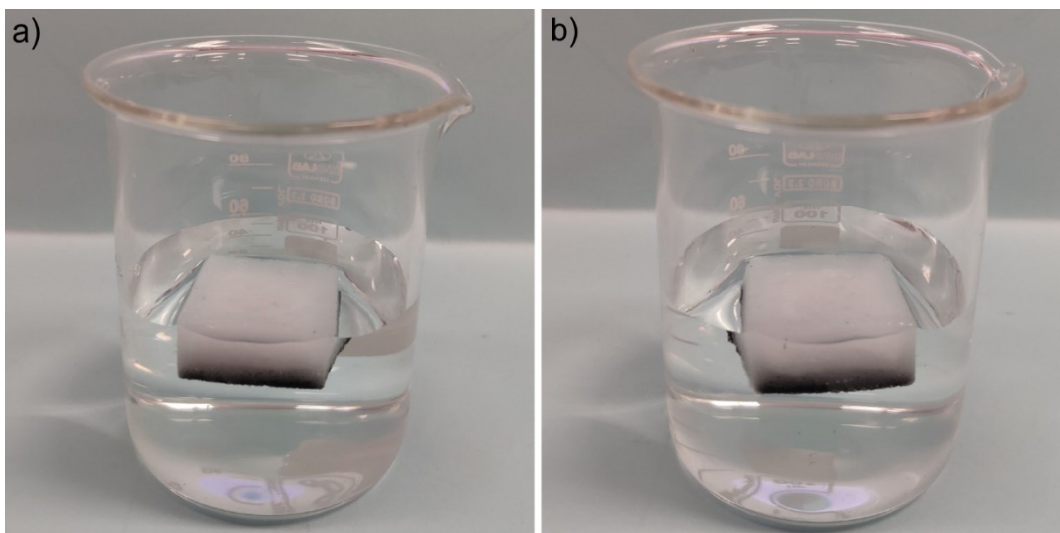


Fig. S13 Photographs of the RS-0.2 (a) before and (b) after 15 mins of sonication.

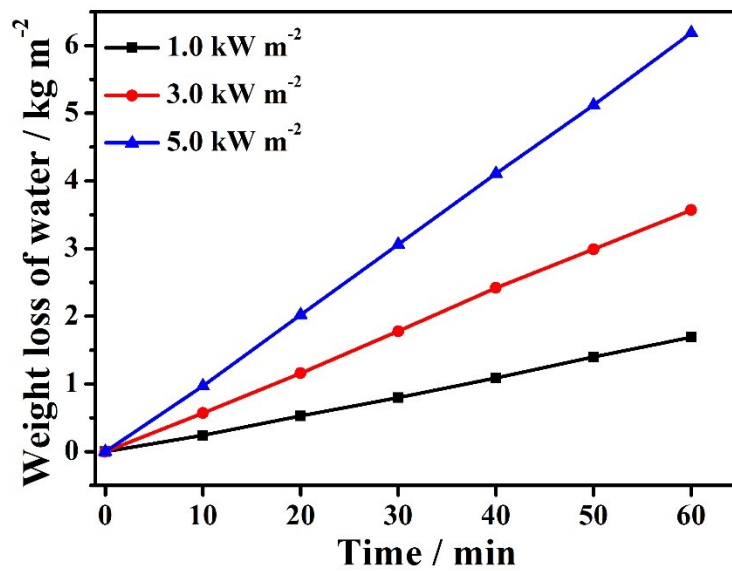


Fig. S14 Time-dependent weight loss of water in the presence of RS-0.20 under 1.0, 3.0 and 5.0 sun irradiation.

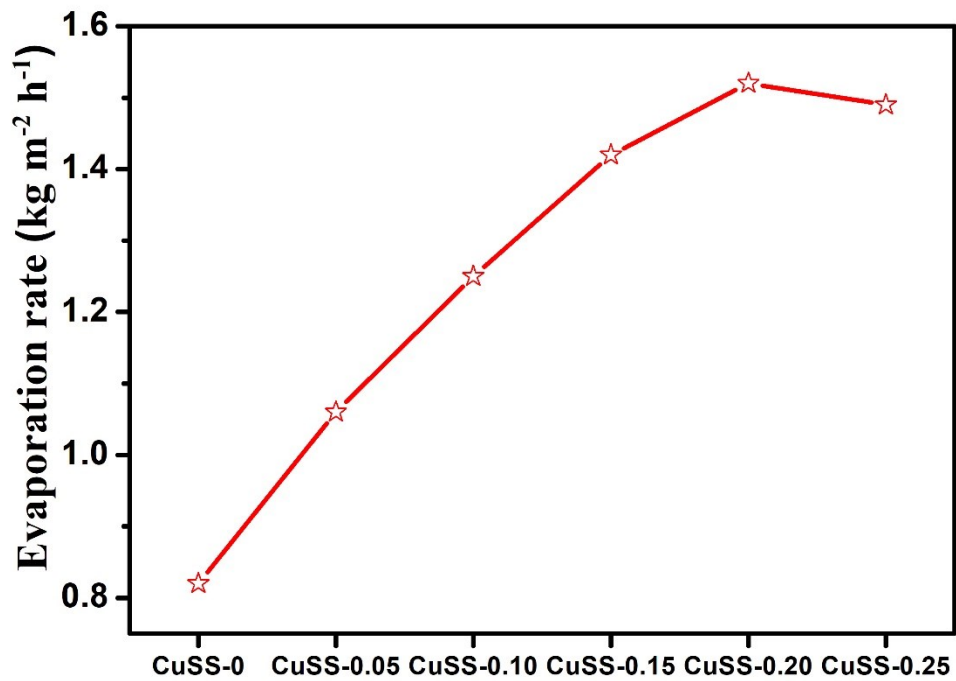


Fig. S15 Evaporation rates of the CuS coated sponges prepared by normal drop-casting (CuSS-0) and interfacial gelation drop-casting (CuSS-0.05, CuSS-0.10, CuSS-0.15, CuSS-0.20 and CuSS-0.25).

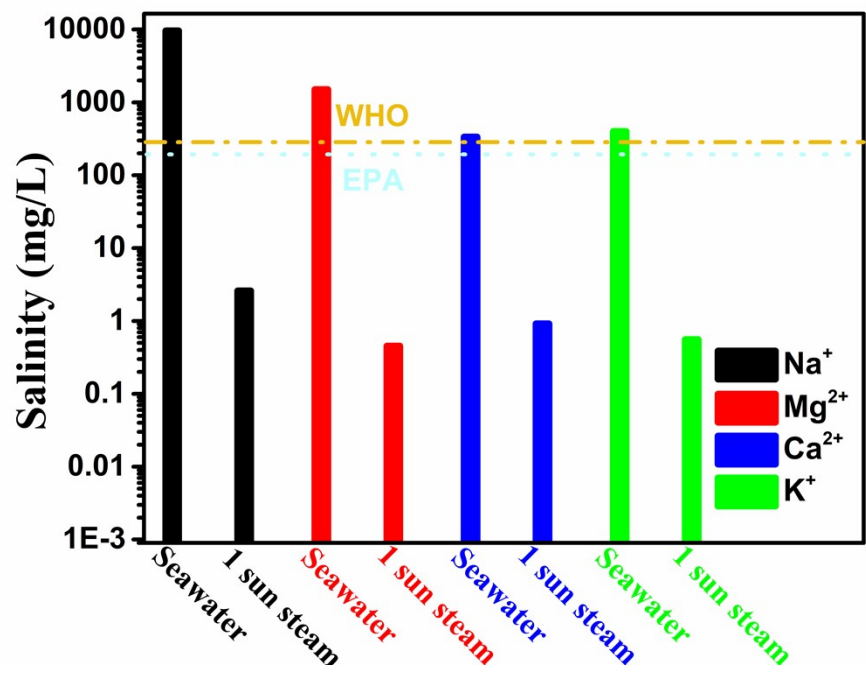


Fig. S16 Major salt ion concentrations of the original seawater and the collected clean water from solar evaporation using the rGO-SA coated sponge (RS-0.20).

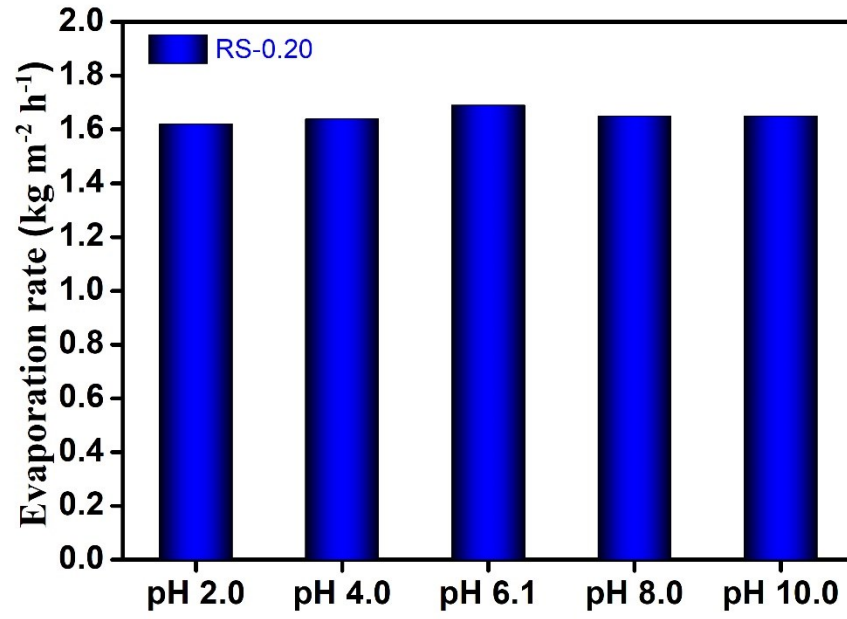


Fig. 17 Evaporation rates of the RS-0.20 under 1.0 sun with water at pH 2.0, 4.0, 6.1, 8.0 and 10.0.