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Anti-biofouling double-layered unidirectional scaffold for long-term solar-driven water evaporation

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Experimental Section

Materials. Experimental Details. Graphite was purchased from Sigma-Aldrich. $NaNO_3$, H_2SO_4, $KMnO_4$, H_2O_2 were purchased from Sinopharm Chemical Reagent Co. Chitosan (CS, viscosity < 400 mPa.s), ZnO nanoparticles (NPs) (20 nm in diameter) were purchased from Aladdin (Shanghai, China). All the reagents were used without further purification.

Characterization. SEM was performed on a Zeiss Merlin compact at 5 kV. TEM was performed on a Hitachi HT7700 at an acceleration voltage of 100 KV. Wide-angle XRD were performed on a Philips X'Pert PRO SUPER X-ray diffractometer. X-ray photoelectron spectra (XPS) were performed on a Thermo ESCALAB250xi. Fourier transform infrared spectra were carried out on a Thermo Nicolet 67 instrument using KBr discs in 500-4000 cm^{-1} region. Compression test was measured on a Instron 5565A mechanical testing system at a load speed of 1 mm/min. The surface area was measured by the BET method using Autosorb-IQ3. Thermogravimetric analyses were performed on Mettler Toledo TGA2 using the temperature range from 30 to 800 ^oC with a heating rate 10 ^oC/min under N_2 atmosphere.

Fabrication of chitosan/ZnO aerogel. 2 g of chitosan powder was dissolved in 100 mL of 1 % acetic acid solution under magnetic stirring overnight. Then the pH of chitosan solution was adjusted to nearly neutral by the addition of 1 % sodium hydroxide solution. Then ZnO nanoparticles aqueous suspension (2 mg/mL) was added dropwise and followed by stirring overnight. The obtained chitosan/ZnO mixture was poured into a silicon rubber mold placed at the top of a liquid nitrogen cooled cold metallic plate, and followed by freezing for 30 min. The frozen samples were lyophilized to obtain porous chitosan/ZnO aerogel. Pure chitosan aerogel was prepared by the same method.

Fabrication of GO-chitosan/ZnO double layered scaffold.
GO aerogel was prepared according to the Li et al' method.[1] After two steps of reduction and freeze, GO aerogel could be obtained at first. Then, chitosan/ZnO mixture was poured into a glass vial, and the preformed GO aerogel was put into this chitosan/ZnO mixture in the top. The glass vial with GO aerogel and the chitosan/ZnO mixture was frozen on a liquid nitrogen cooled cold metallic plate for 30 min and further lyophilized completely to obtain a unidirectional porous double layered aerogel scaffold. Typically, the thicknesses of chitosan-ZnO composite layer and GO layer are 1.0 and 0.5 cm, respectively, and the diameters of the chitosan-ZnO composite layer and GO layer are 1.9 and 1.6 cm, respectively.

Antibacterial test. To evaluate the antibacterial ability of the aerogel scaffolds, samples were cultivated in Luria-Bertani (LB) broth supplemented with bacteria (*E. coli* and *S. aureus*) at the concentration of 10^5 CFU/mL. Bacterial growth was monitored by measuring the optical density (OD) values of the LB broth at 600 nm at the given intervals.

Characterization of the anti-biofouling property of GCZ scaffold. The chitosan/ZnO aerogel and ZnO-free chitosan aerogel were cultivated in bacterial suspensions (*E. coli* and *S. aureus*) at 37 ^{o}C for 72 h. For SEM observation, aerogel samples were washed with normal saline after 48 h, then fixed with 4 % paraformaldehyde in time and subjected to lyophilization. Then, SEM was performed on a Zeiss Merlin compact at 5 kV. For the observation with a confocal laser scanning microscope (CLSM), aerogel samples were took out from bacterial suspensions, and washed with normal saline without further treatment, which were stained by calcein-AM and propidium iodide (PI) for 15 min at 37 °C in dark. Then, an upright fluorescence microscope (Nikon 80i Eclipse, Japan) at certain wavelengths (490 nm for calcein-AM at and 545 nm for propidium iodide) was used to collect the CLSM images. In addition, The chitosan/ZnO aerogel and ZnO-free GC aerogel were soaked in the lake water (collected from the lake in the campus of South China University of Technology, Guangzhou, China) for 10 days at 30^{o}C to evaluate the formation of biofilm in natural water.

Solar-driven water evaporation evaluation. The solar beam was simulated by a Xenon lamp. The power density of the illumination on the floating aerogel surface was regulated to 10 kW m^{-2}. The photothermal evaporation area is approximately 2 cm^2 for the GO aerogel. During the illumination, the temperature was recorded by an IR camera (Fluke Ti300), and the evaporation mediated weight loss of water was recorded by an electronic balance (Mettler Toledo AL204) at the same time. To evaluate the effect of biofouling on the solar-driven water evaporation efficiency of the scaffolds, the antifouling GCZ scaffold and ZnO-free chitosan scaffold were cultivated in bacterial suspensions (*E. coli* and *S. aureus*) for 72 h, then they were took out to measure the water evaporation performance as above. In order to investigate the photothermal evaporation property of the scaffold in natural water, the GCZ scaffold and ZnO-free GC scaffold were cultivated in lake water for 10 days, then they were took out to measure the photothermal evaporation property under 1 kW/m^2.

Reference

1. L. Qiu, J. Z. Liu, S. L. Chang, Y. Wu and D. Li, *Nat. Commun.*, 2012, **3**, 1241.

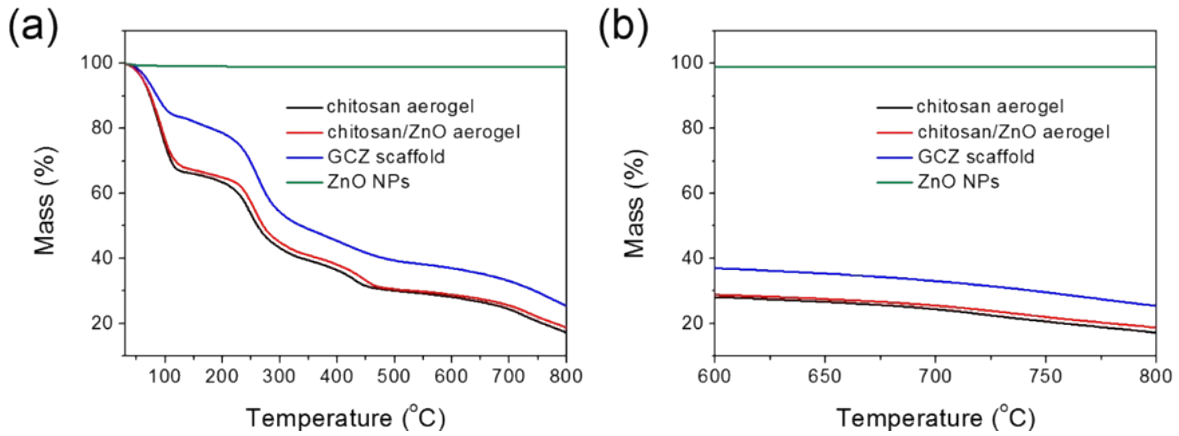

Fig. S1 (a) The TGA curves of chitosan aerogel, chitosan/ZnO aerogel, GCZ scaffold and ZnO nanoparticles under N_2 atmosphere with the temperature rising rate of 10 °C/min. According to the weight losses of ZnO NPs, chitosan aerogel and chitosan/ZnO aerogel, the content of ZnO is calculated to be approximate 1.7 %. (b) TGA curves in the temperature range between 600-800 °C.

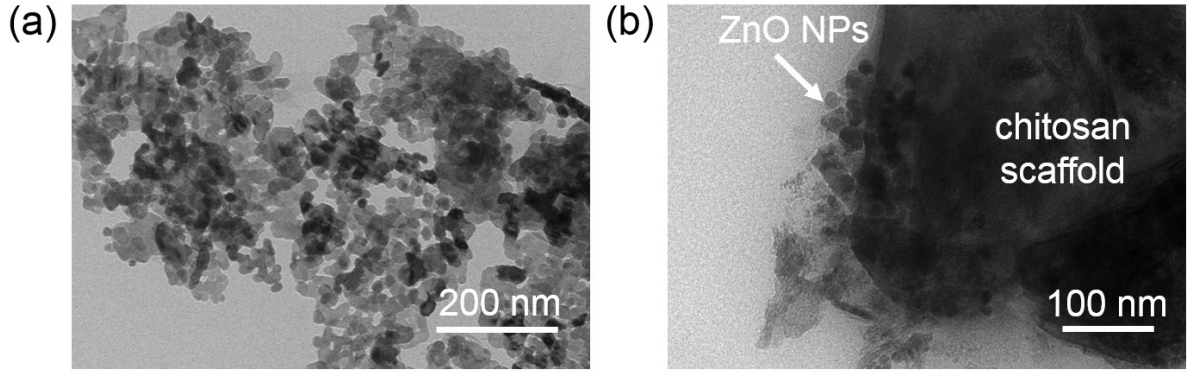

Fig. S2 (a) TEM image of ZnO nanoparticles in the size of about 20nm. (b) In the TEM image of CZ scaffold, ZnO nanoparticles could be identified. To evaluate the stability of the aerogel scaffold, CZ scaffolds with 2.4 mg ZnO were placed in 15 mL water and shaken for 7 days, and the zinc concentration in water was measured by ICP-AES. The leakage rate of ZnO compared to the total ZnO in CZ scaffold was calculated to be 0.28%.

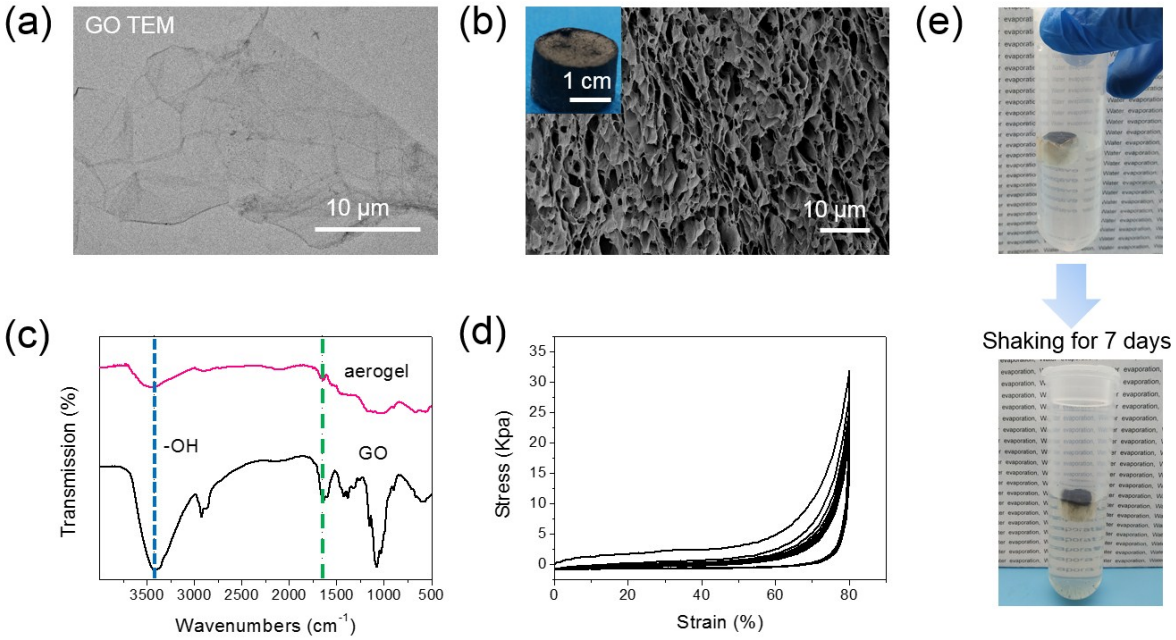

Fig. S3 (a) TEM image of GO nanosheets. (b) The digital photo and SEM image of the obtained GO aerogel. (c) FT-IR spectra of GO powder and the obtained GO aerogel. (d) Compression properties of the obtained GO aerogel. (e) Digital photos of the double-layer aerogel which placed in a tube filled with water in a shaker at 100rpm for 7 days.

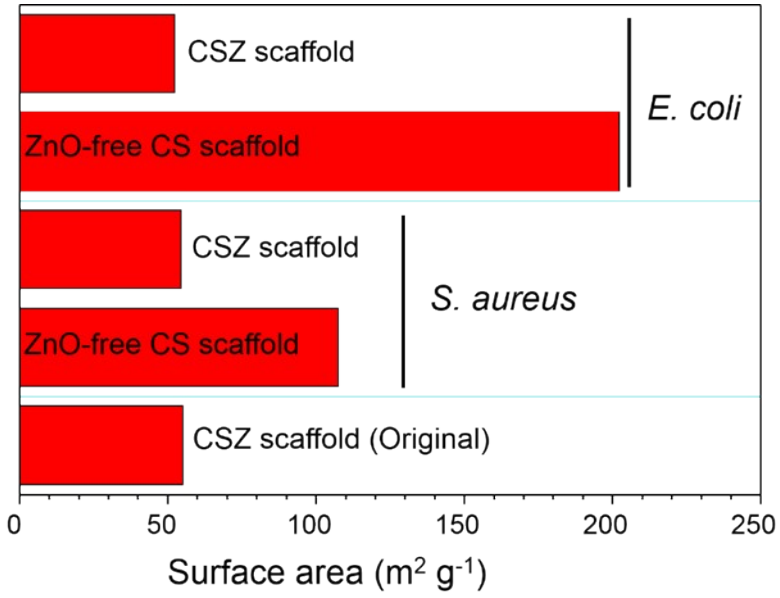

Fig. S4 BET surface area values of CSZ aerogel (Original), and CSZ and ZnO-free CS aerogels after cultivated in bacterial suspensions.

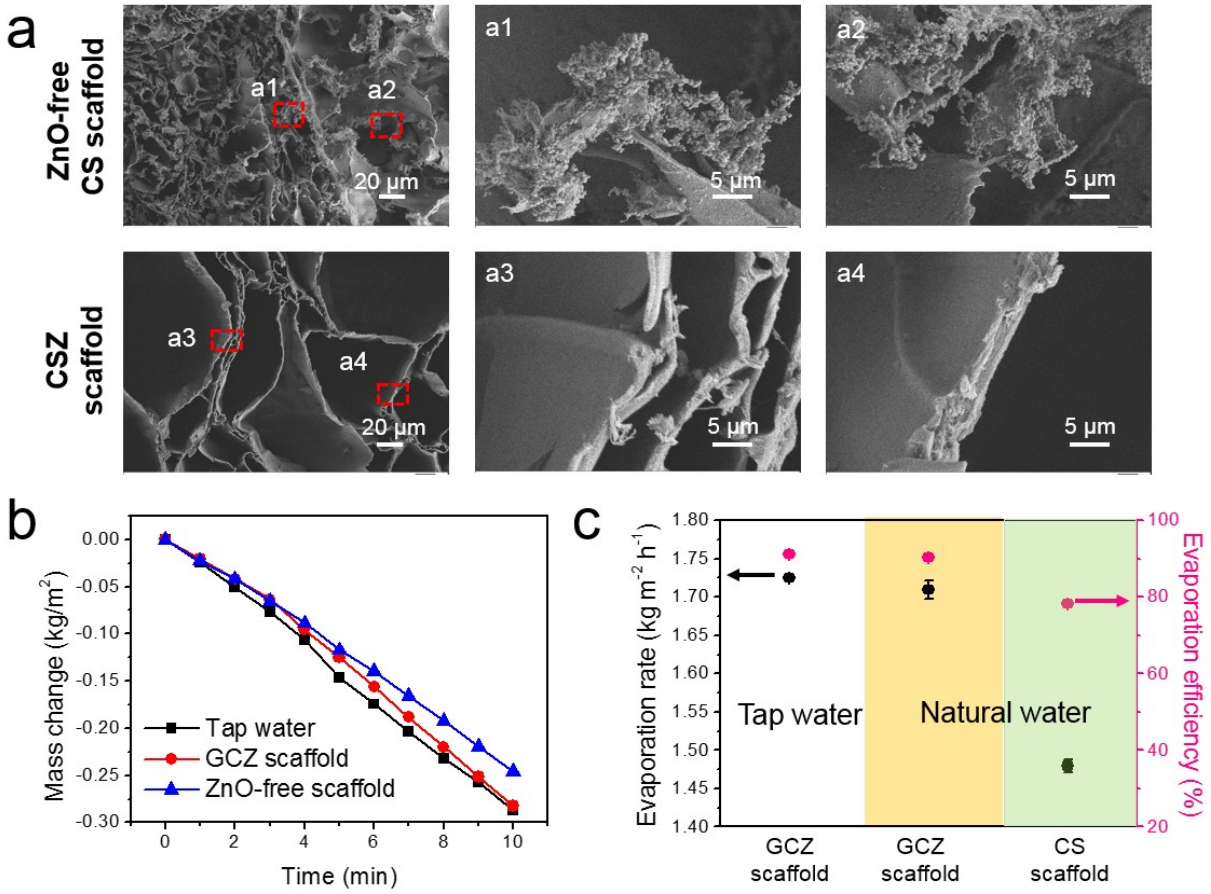

Fig. S5 (a) SEM images of CSZ and CS aerogels after incubated in lake water for 10 days (b) Evaporation induced mass change with different samples under one sun (c) Water evaporation rate (left vertical axis) and evaporation efficiency (right vertical axis) of the anti-biofouling GCZ scaffold and ZnO-free GC scaffold under one sun.

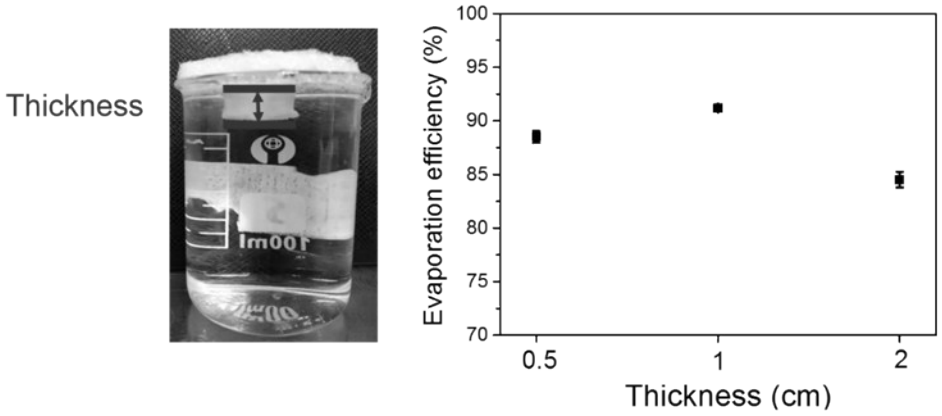

Fig. S6 The evaporation efficiency of GCZ scaffold with different CZ thicknesses under one sun.