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Efficient solar domestic and industrial sewage purification via polymer wastewater collector

Tingzhou Yang^{b,c,1}, Sai Wang^{b,1}, Daniele Benetti^c, Kanghong Wang^{b,c}, Yawen Sun^b, Haoqing Ji^b, Tao Qian^{a,b,*}, Chenglin Yan^b, Federico Rosei^{c,*}

^a School of Chemistry and Chemical Engineering, Nantong University, Nantong 226019, PR China

^b College of Energy, Key Laboratory of Advanced Carbon Materials and Wearable Energy Technologies of Jiangsu Province, Key Laboratory of Advanced Optical Manufacturing Technologies of Jiangsu Province & Key Laboratory of Modern Optical Technologies of Education Ministry of China, Soochow University, Suzhou 215006, PR China

^c Institut National de La Recherche Scientifique, Centre Énergie, Matériaux Et Télécommunications, 1650 Boul. Lionel Boulet, J3X 1S2 Varennes, Québec, Canada

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ABSTRACT

Water pollution caused by domestic and industrial sewage exacerbates the shortage of freshwater, with major negative consequences for society and the environment. Solar-to-steam energy conversion systems, namely the extraction of steam using solar energy, are a promising eco-friendly and cost-effective approach for water purification. However, current technologies still exhibit low efficiency and high energy consumption. Here we report a polymer wastewater collector with a cross-scale hierarchical structure based on Defective polypyrrole-modified activated carbon paper substrate (DPAC), and its use for sporadic wastewater collection and efficient solar-driven sewage purification. Strong absorption of the solar spectrum at an arbitrary incident angle was achieved, which continuously provides heat for evaporation. Water molecules are prone to aggregate around the defective polypyrrole networks, where the generated heat is directly transferred to the water molecules, resulting in a low heat loss and high conversion efficiency for purifying seawater. In addition, DPAC exhibits superior domestic and industrial sewage evaporation rates of 1.37 and 1.28 kg m⁻²h⁻¹ under one sun irradiation with corresponding solar-to-steam conversion efficiencies of 91.8% and 85.8%, respectively. The principle of this solar steam generator may provide useful insights towards the efficient and energy-saving treatment of domestic and industrial sewage.

1. Introduction

Due to the unprecedented industrialization and economic growth experienced during the past three decades, the environment in some developing countries has severely deteriorated. In this framework, the increasing amounts of domestic and industrial sewage cannot be properly treated, exacerbating the water pollution problem [1,2]. In 2019, the challenge of effectively recycling and purifying sporadic contaminated water used for firefighting following the explosion of a chemical plant in eastern China sparked widespread concern for its environmental impact. Ignoring this issue is not an option, as it would lead to secondary pollution through surface water seepage and groundwater movements. Current technologies for sewage treatment focus on using membranes (reverse osmosis and nanofiltration), thermal processes (multi-effect

distillation, evaporation, and crystallization), or biochemical and chemical processes [2-4]. Among these, solar-driven water evaporation is considered particularly promising, since it is environmentally friendly and energy-saving [5-15]. However, most of the recently reported strategies based on the latter technology still suffer from low energy conversion efficiency, due to severe irreversible thermal losses and inefficient solar absorption [9,15]. Furthermore, challenges remain in terms of poor material stability in a water-containing environment, unsatisfactory extraction efficiency for sewage, relatively low transport rate, inferior water harvesting, and transport capabilities [16].

So far various photothermal materials, such as plasmonic metals, semiconductors, carbon-based materials and metallic particles, have been explored for solar-driven water evaporation [5-33]. Although most such systems can convert solar energy into heat, the ideal photothermal

* Corresponding authors at: School of Chemistry and Chemical Engineering, Nantong University, Nantong 226019, PR China (T. Qian).

E-mail addresses: qiantao@ntu.edu.cn (T. Qian), rosei@emt.inrs.ca (F. Rosei).

¹ These authors contributed equally to this work.

material for solar sewage purification must combine poor thermal conductivity, broad absorption and low-cost fabrication for rapid water transportation. However, compared with inorganic materials, the direct use of polymers in solar-driven water evaporation is generally limited by their poor durability, limited hydrophilic properties, and low solar-to-thermal conversion efficiency [17]. A combination of substrates with polymers has been investigated to improve sunlight absorption and prevent heat loss, such as polystyrene foams, polyacrylamide aerogel, polyaniline foams, polymethylmethacrylate layer and polyacrylonitrile layer, which are known as photothermal materials with high stability [3,16-22]. In addition, thermal conductivity can be effectively reduced through polymer encapsulation [16], and the main strategy based on polymers to improve the solar-to-thermal conversion efficiency is to emphasize broadband light absorption, realize thermal manipulation, and build unique nanostructures with minimized transmittance and reflection [17].

Herein, we report the fabrication of a wastewater collector based on Defective polypyrrole-modified activated carbon paper substrate (DPAC) with a cross-scale hierarchical structure for excellent water harvesting capability and high-efficiency solar-driven sewage purification (Fig. 1a). The hierarchical microstructure of Activated carbon paper (ACP) can induce refraction and scattering inside the evaporator and let DPAC enable a high solar absorptivity at an arbitrary incident angle, further reducing the reflective energy loss. The defective polypyrrole network with unique nanostructure results in a broadband light absorption and can capture and confine the water molecules, where the generated heat is directly transferred to the water molecules, minimizing the heat loss and promoting high solar-to-steam conversion efficiency. When used for solar sewage purification under one sun irradiation, the DPAC exhibits superior domestic and industrial sewage evaporation rates of 1.37 and 1.28 kg m⁻²h⁻¹, corresponding to a solar-to-steam conversion efficiency of 91.8% and 85.8%, respectively. These results demonstrate that our sewage collection and evaporation strategy leads to highly efficient and stable water purification.

2. Experimental section

2.1. Preparation of DPAC

Commercial graphite sheet carbon paper was bought from the Kexing carbon Co., Ltd, and washed with ethanol before use. KMnO₄ (6 g) was slowly added to the mixture solution containing concentrated H₂SO₄ (98%) and concentrated HNO₃ (68%) at -2 °C. Then, four pieces of CP (2.8–3.0 cm in diameter) were immersed in the mixture, and the reaction system was transferred and kept at 35 °C for 6 h. Distilled water was added to the mixture drop by drop, and the H₂O₂ solution was added dropwise to the mixture until no gas bubbles evolved. After washing with diluted hydrochloric acid (10%) and distilled water, the ACP was dried by the vacuum freeze drier. The DPAC was prepared by the addition of 15 mL H₂O₂ to the ACP/pyrrole/FeCl₂/H₂O (1.0 piece/2 mL/0.2 g/383 mL) mixture and allowed to stand for 6 h. The TPAC was prepared by the mixture of ACP, octyltrimethylammonium bromide (OTAB), ferric chloride, and pyrrole.

2.2. Preparation of artificial domestic and industrial sewage

Seawater was collected from the East China Sea (33 psu). A mixture of Glucose (11.5 g), CH₃COONa (15.4 g), NaCl (26.7 g), NH₄Cl (5.4 g), KH₂PO₄ (1.8 g), MgSO₄ (5.5 g), Yeast extract (5.8 g), and edible oil (4 wt %) was dissolved in deionized water (1.0 L) to obtain artificial domestic sewage. The artificial industrial sewage consisted of 5.0 M Direct Red (CAS:2619-10-8), 5.0 M Direct Blue (2429-74-5), and 5.0 M Direct Black (CAS: 6428-31-5).

2.3. Characterization

The morphology and structure of the solar absorber were characterized by field emission scanning electron microscopy (SU8010, Hitachi, Ltd) and field-emission transmission electron microscopy (FEI Tecnai G220, FEI NanoPorts, Ltd). The transmittance and reflectance were measured by UV-vis-NIR Lambda 750S and Agilent Cary 5000 with Universal Measurement Accessory (UMA). Raman spectra were recorded on an HR Evolution (Horiba Jobin Yvon) Raman spectrometer.

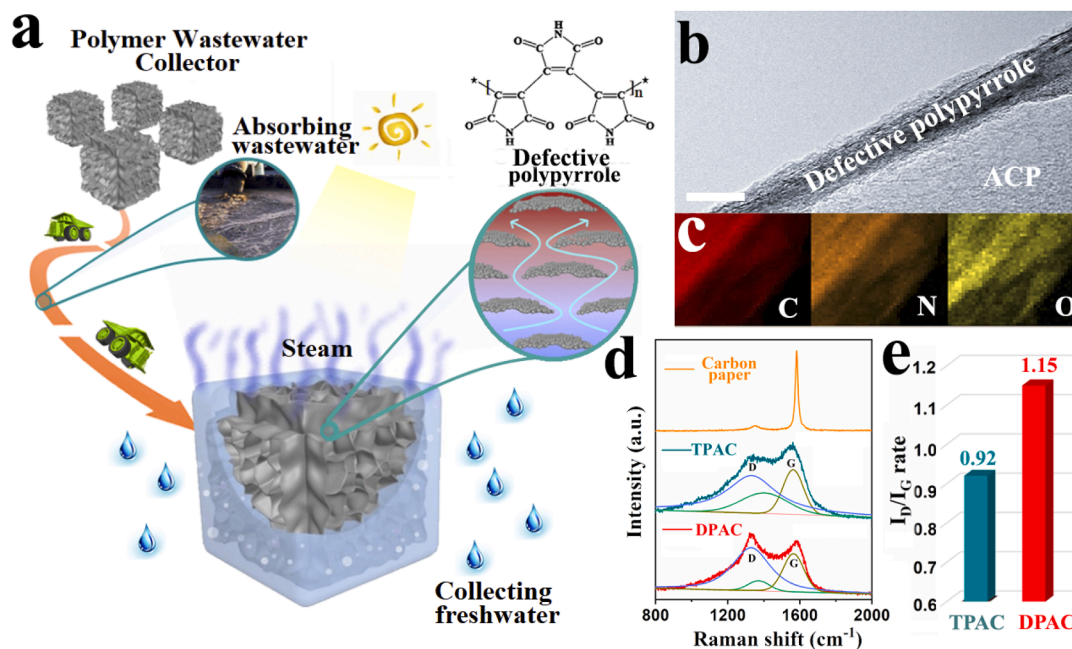


Fig. 1. Schematic and morphology of water collector and solar water purification. (a) Schematic of the evaporation process of polymer wastewater collector. (b) TEM image of DPAC. Scale bar, 10 nm. (c) The corresponding EDX mapping images of C, N, and O element distributions. (d) Raman spectra of the different solar water evaporators. (e) Variation in the intensity rate of the D and G bands.

Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet 50 spectrometer (Thermo Fisher Scientific, America). Surface elemental analysis was performed with an X-ray photoelectron spectrometer (XPS, Escalab 250Xi, Thermo Fisher, America).

2.4. Water extraction from sewage and seawater

The evaporator was irradiated using a solar simulator (XES-70S1) equipped with a xenon lamp controller. Ambient humidity was maintained at 40%-42%. The absorbers were floated in a glass Petri dish (3 cm in diameter) filled with sewage or seawater. The sunlight was perpendicularly incident to the top surface of absorbers, and the evaporating surface was placed at a distance of 20 cm from the lamp. Before each measurement, the optical intensity at the evaporating surface was monitored and adjusted to 1.0 kW m^{-2} . The weight loss was measured using an electronic balance (BS114S, Sartorius), and the surface temperature of the absorbers was determined with infrared imaging (Flir EX4 infrared camera) and a rodlike hot junction thermocouple (Anritsu Meter Co. Ltd., Japan). All the tests were repeated more than three times, and the average was used as the final value to reduce the errors. First, we record the evaporation capacity of seawater without any evaporator at the same conditions (Fig. S1). The evaporation capacity was obtained by subtracting the bare seawater evaporation capacity from the tested value. The obtained evaporation capacity is used to calculate the solar-to-steam conversion efficiency.

2.5. Computational method

Molecular dynamics (MD) simulations were performed with Gromacs, version 5.0.5. The object systems were constructed by randomly dispersing 5 graphene and defective polypyrrole molecules into 5000 water molecules. Graphene and defective polypyrrole were modeled using the OPLS-AA force field [34], with the parameters generated by the LigParGen server [35]. Water was described by the SPC/E model [36]. VDW interactions were described by the Lennard Jones (LJ) potential, which was truncated at 1.2 nm. The LJ parameters for unlike atom pairs were derived by the geometric combination rules. Electrostatic interactions were calculated using the particle mesh Ewald algorithm with a real space cut off of 1.2 nm, while the long-range part was calculated in reciprocal space with a Fourier spacing of 0.12 nm. The equations of motion during simulations were integrated with the leap-frog algorithm using a time-step of 1 fs. Energy minimization was first carried out by the steepest descent algorithm to remove any bad contact during model construction. Subsequently, isothermal-isobaric equilibrium at 298.15 K/1 bar was performed for 50 ps, then 20-ns MD runs were carried out under NPT ensemble, with the system temperature and pressure controlled by the Nose-Hoover thermostat and Parrinello-Rahman barostat, respectively. 3D periodic boundary conditions were applied throughout simulations.

3. Results and discussion

We prepared a defective polypyrrole-modified activated carbon paper via *in situ* polymerization. The Activated carbon paper (ACP) was fabricated by a strong oxidizing process of commercial Carbon paper (CP, Fig. S2). The obtained ACP substrate exhibited improved hydrophilicity, due to the generation of the hydroxyl and carboxylic groups and the interruption of the original adjacent aromatic lattice on graphite, which created a loose lamellar morphology (Fig. S3). The nano-interspace between each carbon sheet inside the hydrophilic ACP can service as fast water transport channels during the solar-water evaporation. Subsequently, defective polypyrrole was uniformly distributed on the lamellar structure of the ACP substrate via *in situ* polymerization, establishing a unique evaporative surface from the nanoscale (nanostructure of defective polypyrrole) to the macroscale (hydrophilic structure of ACP), which was further confirmed by

Transmission electron microscopy (TEM), Scanning electron microscopy (SEM) and Energy dispersive X-ray (EDX) analysis (Fig. 1b-c and S4-5). The cross-scale hierarchical structure can effectively regulate the thermal concentration and water content, focusing heat at the nanobranches of DPAC [17]. Compared with Traditional polypyrrole (TPAC), the Fourier transform infrared spectrum of DPAC exhibits a weak absorption peak at 1700 cm^{-1} (Fig. S6), which is attributed to C=O. The results indicated that carbonyl defects incorporated into polypyrrole, which was confirmed by X-ray photoelectron spectroscopy (XPS, Fig. S7). The C 1s XPS spectrum is fitted with four components corresponding to the C=C, C-C, C-N, and C=O bonds. The considerable amount of carbonyl defects in defective polypyrrole were further confirmed by the intensity ratio of the D and G bands in Raman analysis (Fig. 1d and S8). Both spectra of TPAC and DPAC exhibit two strong bands and one broadband. Two strong peaks located at 1331 and 1567 cm^{-1} can be indexed as D-band (the disordered $\text{sp}^3\text{-C}$ atoms) and G-band (the in-plane bond-stretching motion of pairs of $\text{sp}^2\text{-C}$ atoms), respectively. The extra low-intensity peak ascribes to the vibration from the edge atoms [37]. Different from TPAC with the high regularity of pyrrole structure and relatively fewer defects, our methods result in a further increase in defects for polypyrrole as shown by the higher I_D/I_G ratio of DPAC compared with TPAC (1.15 vs. 0.92, Fig. 1e), suggesting the widespread formation of carbonyl defects. The defect-related properties of DPAC have been widely studied and are attributed to their enhanced hydrophilic properties with polar functional groups [38-40], which exhibit great potential for solar water purification.

As shown in Fig. 2a, the thickness of dry DPAC expanded from 0.5 to 8.3 mm, indicating that the volume of DPAC mostly contributed by the holes of varying size was about 16.6 times larger than that of the carbon paper. The unique cross-scale hierarchical structure from the nanoscale to the macroscale and extended volume endows DPAC with enough

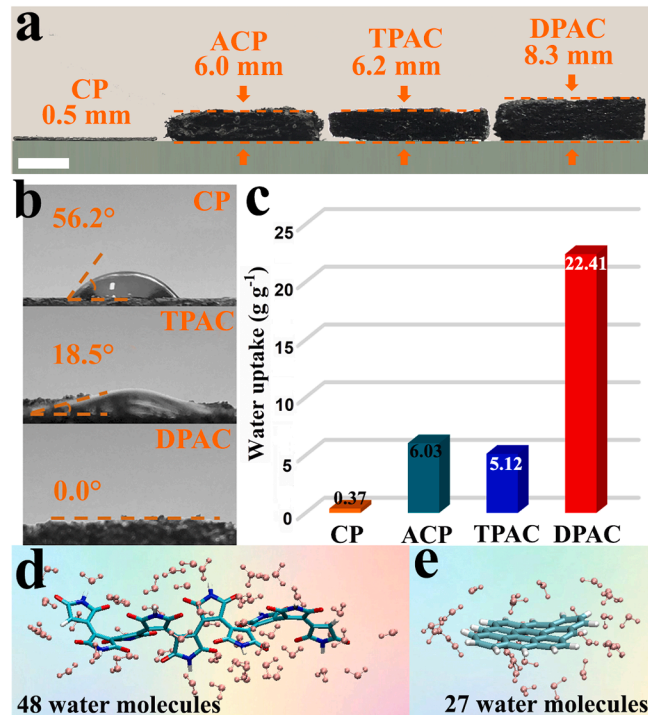


Fig. 2. Water-holding capacity and superhydrophilic property. (a) The comparison of volume change between CP, ACP, TPAC, and DPAC. Scale bar: 10 mm. (b) The comparison of contact angles of different polymer wastewater collectors, which enables good water wicking ability. (c) The comparison of water-holding capacity between CP, ACP, TPAC, and DPAC. Computer simulation of the distribution of water molecules within 3 Å from (d) polypyrrole chain and (e) carbon sheet.

interconnected water channels, wrinkled internal surface, and more evaporating surface. Furthermore, carbonyl groups are hydrophilic, the carbonyl defects on the surface of defective polypyrrole can further improve the hydrophilicity of DPAC. As shown in Fig. 2b and S9, the CP shows a water contact angle of 56.2° , and TPAC presents hydrophilic surfaces with a contact angle around 18.5° . The DPAC can be easily wetted by the water droplet and rapidly absorb it in less than one second, exhibiting a superhydrophilic property. The fast water transport performance of DPAC is shown in Fig. S10. Due to its superhydrophilicity, DPAC absorbs water for only 0.78 s to cover the whole 8.0 cm^{-2} surface, which is much faster than that of ACP (0.96 s) and TPAC (1.62 s). At the same time, superhydrophilic materials usually exhibit underwater superoleophobic properties. When covering water with oil, the DPAC can pass through the oil and rapidly absorb the water in the lower layer (Fig. S11). Due to its strong water-absorbing capacity, fast water transport performance, and excellent wettability, the DPAC can efficiently replenish water molecules during solar evaporation. Compared with CP (0 g min^{-1}), ACP (5.37 g min^{-1}), and TPAC (3.61 g min^{-1}), DPAC exhibited a high water flow rate up to 7.56 g min^{-1} (Fig. S12). The DPAC with a cross-scale hierarchical structure also can improve the water harvesting capability, defined as the total amount of water that can be absorbed per gram of a polymer wastewater collector. In Fig. 2c, only 0.89 g water can be absorbed into 2.4 g CP corresponding to a water-holding capacity of 0.37 g g^{-1} , due to the small volume and poor hydrophilicity. The water-holding capacity of the ACP is still low, only reaching about 6.03 g g^{-1} . This is due to the fact that the π - π stacking between un-oxidized aromatic regions in the ACP limits the increase of the hole-contributing volume, resulting in a low water-holding capacity. The coating of traditional polypyrrole reduces the hydrophilicity of the material, leading to a decline in water-holding capacity (5.12 g g^{-1}). On the other hand, the large volume of DPAC and the excellent hydrophilicity derived from high defect concentration endowed the polymerized polypyrrole networks inside the DPAC to capture water and confine the water on the surface, exhibiting an extremely high water-holding capacity, up to values of 22.41 g g^{-1} , which is 60.6, 3.7, and 4.4 times higher than that of the CP, ACP, and TPAC, respectively. Due to its excellent water harvesting capability and water absorption capacity, the DPAC can be used to collect and confine the sporadic wastewater, which is hard for large-scale recycling, preventing wastewater from seeping into groundwater and avoiding secondary pollution. We further investigated the dynamic distribution of water molecules between the normal carbon sheets and defective polypyrrole chain using Molecular dynamics (MD) simulations. During model construction, five defective polypyrrole chains and carbon sheets were placed randomly into a solution with 1000 water molecules. Fig. 2d-e exhibits the aggregation of water molecules within 3 Å from the defective polypyrrole chain and carbon sheet. Not surprisingly, water molecules are prone to aggregate around the defective polypyrrole chain

instead of the carbon sheet. The radial distribution function (RDF) describes the probability of spatial distribution of water molecules at different distances. The RDF of defective polypyrrole chains is higher than that of the carbon sheet (Fig. S13), at the distance between 0.3 and 1.2 nm, further confirming the excellent hygroscopicity of the polymer wastewater collector. Due to its superhydrophilicity, the polymerized polypyrrole networks can capture water and confine the water on the surface of the floating DPAC evaporator, where the generated heat is directly transferred to the water molecules, further leading to high solar-to-steam conversion efficiency and minimizing the heat loss.

The absorption properties of DPAC were investigated by UV-vis-NIR spectroscopy, to assess the solar-thermal conversion. The light absorption of DPAC was measured to be near 99.4% in the 400 to 1000 nm spectral range, which was much higher than that of the CP (40.3%), ACP (66.6%), and TPAC (76.2%). The defective polypyrrole with a unique nanostructure results in a broadband light absorption, which is deficient for CP and ACP (Fig. 3a). We therefore measured the angular-dependent absorbance by UV-vis-NIR spectroscopy [11,41,42]. The ACP shows poor average absorbance (between 400 and 800 nm) as the incident angle increases from 15° to 70° (Fig. 3b). However, the DPAC exhibits much higher average absorbance than the ACP and TPAC, especially at incident angles from 15° to 40° . The introduction of oxygen vacancies can enhance visible light absorption and exhibit a narrower bandgap [40]. In addition, the porous framework of DPAC is suitable to minimize reflection and increase the optical path, and the defective polypyrrole can effectively enhance broadband light absorption due to the closely spaced energy levels of the loosely held π electrons. With the π -conjugated backbones of sp^2 -hybridized carbon, the defective polypyrrole has a controllable bandgap and split energy levels [17], leading to strong light absorption and high light-to-heat conversion efficiency. Moreover, the activated carbon paper with a hierarchical microstructure can induce refraction and scattering inside the evaporator and let DPAC enable strong absorption of the solar spectrum at an arbitrary incident angle, further reducing the reflective energy loss.

This outstanding light absorption translates into the efficient solar-thermal conversion of the DPAC for developing high-efficiency solar water evaporation systems. As shown in Fig. 3c, the surface temperature of dry DPAC increases from 24.3 to 45.8°C within 1.0 min under one sunlight irradiation, which was much higher than values measured for dry CP (24.8°C), ACP (28.1°C), and TPAC (35.1°C). The CP, ACP, and TPAC exhibited low light absorption, corresponding to a high reflective energy loss. From the infrared images of AP and ACP, the heat diffuses into the surrounding large space. For TPAC evaporators, they still meet the challenges of slight heat diffusion. The malposition between heat and evaporator is caused by the serious heat diffusion into the surrounding large space, which cannot be used for efficient solar-thermal conversion. In sharp contrast, the cross-scale hierarchical structure of DPAC allows light with different wavelengths to reflect and transmit

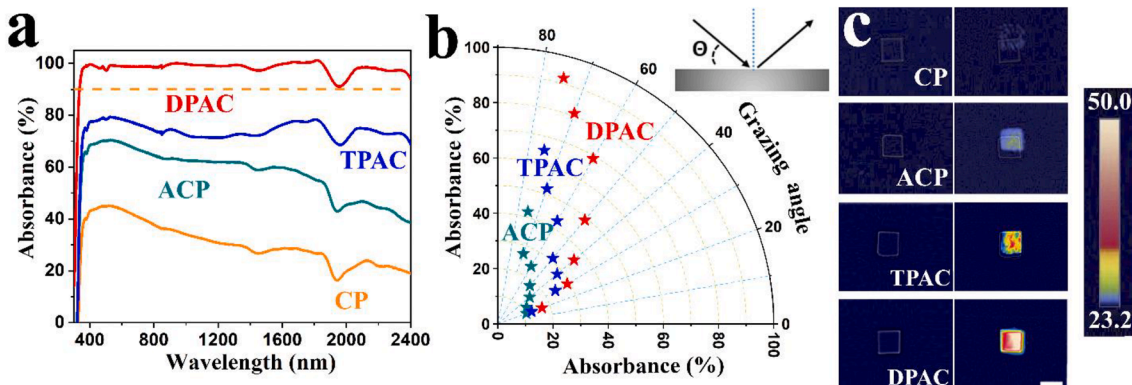


Fig. 3. (a) UV-vis-NIR reflection spectra of the different polymer wastewater collectors. (b) Comparison of the average absorbance between 400 and 800 nm on the incidence angles. (c) Infrared images of the temperature distribution within 1.0 min under 1-sun irradiation. Scale bar: 2.0 cm.

into the carbon skeleton. At the same time, the inner carbon skeleton can broadly absorb light via the continuous energy levels arising from the hybrid bonds, and defective polypyrrole can adequately absorb light and efficiently convert solar energy into heat via molecular vibrations and non-radiative relaxation [43]. The position of the heat for DPAC matched well with the position of the DPAC evaporator. Compared with CP, ACP, and TPAC, the polymer coating endows DPAC with good thermal confinement property, where the generated heat is highly localized on the surface of the DPAC evaporator and no obvious heat diffusion can be observed. Having measured a high water-holding capacity and efficient solar-thermal conversion, we then investigated the evaporation rate and solar vapor conversion efficiency of the DPAC using a homemade evaporation system. The latter is composed of a steam generation chamber and freshwater collection device (Fig. 4a). The DPAC was floating on the surface of seawater or sewage as the evaporator for generating steam, and the vapor condensed into freshwater on the cold wall of the collection device. As shown in Fig. 4b, the mass change varies almost linearly as a function of irradiation time and the evaporation rate can be estimated from the slope. When irradiated with an incident power density of 1.0 kW m^{-2} (one sun irradiation), the bare seawater and the ACP only exhibit a low evaporation rate of $0.10 \text{ kg m}^{-2}\text{h}^{-1}$ and $0.83 \text{ kg m}^{-2}\text{h}^{-1}$. By comparison, the DPAC exhibits a high evaporation rate of $1.41 \text{ kg m}^{-2}\text{h}^{-1}$ because of the defective polypyrrole-modified porous framework and lamellar structure. As shown in Fig. S14, a stable evaporation rate can be maintained for more than 2 days. When the irradiation intensity was varied between $0.8, 1.0$, and 1.5 kW m^{-2} , the DPAC still exhibited a stable evaporation rate of $1.11, 1.41$, and $2.37 \text{ kg m}^{-2}\text{h}^{-1}$, respectively (Fig. 4c). Due to the excellent salt resistance of the evaporator [44-47], the DPAC exhibits a high evaporation rate of 1.39 and $1.32 \text{ kg m}^{-2}\text{h}^{-1}$ under one sun irradiation with a salinity of 35 psu and 105 psu, respectively (Fig. S15). When the system is exposed to the real sunlight (562 W m^{-2}), the average water evaporation rate of the DPAC evaporator is $0.82 \text{ kg m}^{-2}\text{h}^{-1}$ (Fig. S16). From Fig. S17, no Sodium chloride crystals can be

observed from the SEM images after cycles in seawater, further demonstrating the excellent salt resistance of the DPAC evaporator.

A rodlike hot junction thermocouple was used to measure the temperature of the different floating evaporators under one sun irradiation (1.0 kW m^{-2}). As shown in Fig. 4d and Fig. S18, the surface temperature of bare seawater monitored by thermocouple slightly increases from 25°C to 29.1°C , and stabilizes around 30.3°C over time. It can be found that, by involving the ACP or DPAC, the temperature of the wet solar evaporators can increase rapidly from room temperature to a stable plateau of 41.2°C and 51.8°C , respectively, under one sun illumination. This significant solar-thermal conversion effect of the DPAC can be observed from the infrared images irradiated for $0, 20$, and 60 min (Fig. 4e), indicating that the generated heat is highly localized on the surface of the DPAC evaporator. The temperature of the top portion of seawater increases quickly compared with bottom water, which means that the heat is localized where evaporation happens, and the absorbed energy is mainly utilized to heat water. After 60 min, the temperature of DPAC (over 50°C) is much higher than that of the seawater ($\sim 32^\circ\text{C}$) in the beaker and no heat diffuses into the surrounding large space. The temperature of the seawater is in agreement with the temperature change of bare seawater after exposing to the simulated sunlight, further demonstrating that the generated heat is localized on the surface of the DPAC evaporator. At the same time, higher converted temperatures caused the evaporation rate to increase. We subsequently calculated the solar-to-steam conversion efficiency (η) according to the following equation:

$$\eta = \frac{Q_e}{Q_s} = \frac{\dot{m}h_{LV}}{C_{opt}q_i}$$

where $\dot{m}$ is the water evaporation rate and h_{LV} is the total enthalpy of change for the liquid-vapor phase. $C_{opt}q_i$ is the incident light power for the solar absorber. The η of the DPAC is about 94.5% , which is much higher than that of the ACP (55.9%) and the seawater without evaporator (6.7%) (Fig. 4f). The solar-to-steam conversion efficiency of DPAC

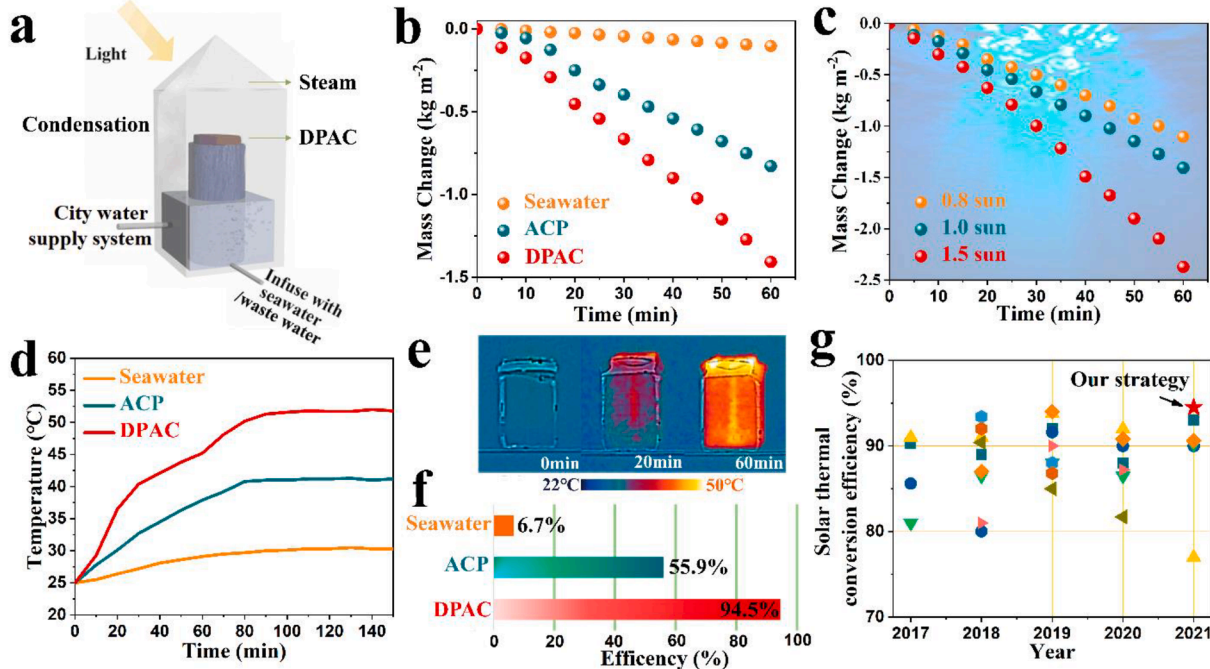


Fig. 4. Efficient and stable water desalination. (a) Schematic illustration of solar steam generation, which can be expanded to accommodate large-scale applications. (b) The mass change of seawater with the light power density of 1.0 kW m^{-2} . (c) The seawater evaporation rate of DPAC with different light power densities. (d) The corresponding temperature distribution during steam generation with the light power density of 1.0 kW m^{-2} . (e) Infrared images of the temperature distribution after illumination. (f) The solar-to-steam conversion efficiency of different absorbers. (g) Comparative results on solar-to-steam conversion efficiency between the evaporator of DPAC and other reported absorbers in the literature [4-36,41-47].

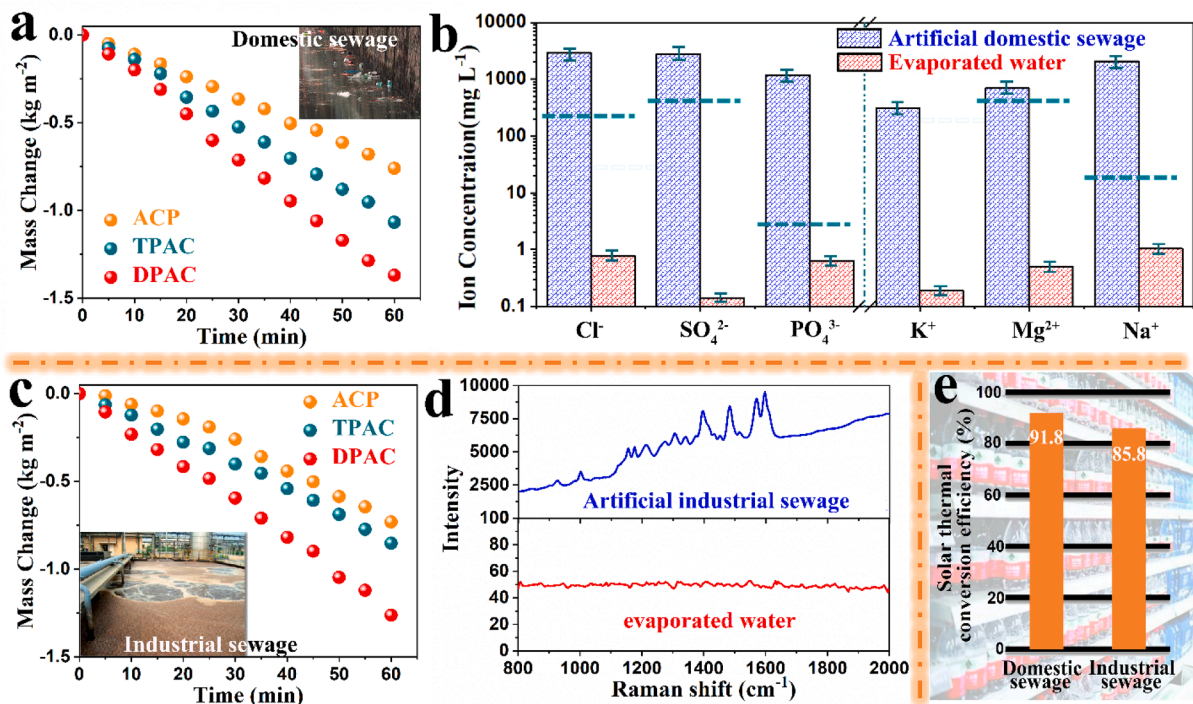


Fig. 5. Efficiency solar water purification. (a) The domestic sewage evaporation rate between ACP, TPAC, and DPAC. (b) Comparison of the concentrations of ions in artificial domestic sewage and evaporated water by DPAC. The dotted line is the corresponding to the WHO standard of drinking water. (c) Comparison of industrial sewage evaporation rate with the light power of 1.0 kW m⁻². (d) Raman spectra of artificial industrial sewage and evaporated water. (e) The solar-to-steam conversion efficiency of DPAC in different sewage.

is much higher than that of previous reports [4–36,41–47], further demonstrating that DPAC has great potential application in sewage purification (Fig. 4g). According to the calculation in Table S2, the sum of all possible energy losses including different kinds of convective heat loss, radiation heat loss, conductive heat loss, and reflection energy loss is 6.8% when under 1 sun illumination.

Finally, DPAC was further applied for the solar-driven purification of domestic and industrial sewage. The large amounts of salt and oil in domestic sewage are prone to cause congestion in the water supply and vapor channel of the evaporator materials, gradually leading to a sharp drop in the evaporation rate and solar-to-steam conversion efficiency. However, DPAC exhibited superhydrophilic properties, making it easy to bind water to form a film on the surface, which could effectively repel the oil, leading to efficient water replenishment. When DPAC was used to purify the domestic sewage comprising 4.0 wt% oil, the evaporation rate reached values of about 1.37 kg m⁻²h⁻¹ (Fig. 5a). In contrast, the ACP and TPAC had much lower evaporation rates of 0.76 and 1.07 kg m⁻²h⁻¹, respectively. Moreover, we captured water vapor using a cold glass and measured the ion concentration of sewage and distilled water using inductively coupled plasma-optical emission spectrometry (ICP-OES) and ion chromatography characterization. Fig. 5b shows that the concentrations of Cl⁻, SO₄²⁻, PO₄³⁻, K⁺, Mg²⁺, and Na⁺ significantly reduce to below 1.0 mg L⁻¹ after the desalination process. After the evaporation and condensation, the ion concentration of obtained purified water is all far below the WHO standard of drinking water.

How to effectively deal with industrial sewage has always been a major challenge in the field of galvanization, plating, and petroleum industry. We also used DPAC to provide a convenient and integrated solution for high sewage harvesting capability and its purification by solar water evaporation (Fig. S19). An artificial equivalent of industrial sewage was prepared specifically by mixing direct dye pollutants, which were high-risk pollutants in major industrial sectors such as printing and textiles. Fig. 5c illustrates that the DPAC yields an industrial sewage evaporation rate of 1.26 kg m⁻²h⁻¹, which is 1.73 and 1.48 times higher

than that obtained from ACP and TPAC. Furthermore, the representative Raman peaks from industrial sewage between 1150 cm⁻¹ and 1600 cm⁻¹ are observed (Fig. S20), which are in accordance with the characteristic vibration peaks of -SO₃ of sulfonic acid group, -N=N- of azobenzene group, and -C=C- of the aromatic ring [6]. As shown in Fig. 5d, no representative peaks can be observed from the Raman spectrum of distilled water. Notably, our strategy could also exhibit stable performance during the cycle tests for solar domestic and industrial sewage purification, which exhibit a high evaporation capacity of 1.37 and 1.28 kg m⁻²h⁻¹ during the 10 h continuous test under one sun irradiation (Fig. S21). The DPAC shows a significant enhancement of the sewage evaporation rate, and the solar-to-steam conversion efficiency is around 91.8% for domestic sewage and 85.8% for industrial sewage (Fig. 5e). These results confirm that DPAC has great potential for the purification of domestic and industrial sewage. We further investigate the structural stability under extremely acidic conditions by SEM imaging (Fig. S22). There is no significant structural collapse and crack after three cycles of more than 30 h, which further demonstrate the excellent durability of our strategy in highly corrosive sewage.

4. Conclusions

In summary, we report the design and fabrication of a polymer wastewater collector based on defective polypyrrole-modified activated carbon paper and demonstrate its performance for water harvesting capability and efficient solar-driven sewage purification. DPAC can be used to spontaneously collect sporadic sewage due to its high water-holding capacity. Thanks to the cross-scale hierarchical structure, DPAC affords strong solar absorption at an arbitrary incident angle, further reducing the reflective energy loss. The polymer networks can capture and confine the water on the surface of the floating DPAC evaporator, where the generated heat is directly transferred to the water molecules, leading to a high solar-to-steam conversion efficiency (94.5%). As a result, we obtain superior long-term domestic and

industrial sewage evaporation rates of 1.37 and 1.28 kg m⁻²h⁻¹ with a corresponding solar-to-steam conversion efficiency of 91.8% and 85.8%, respectively. Therefore, given the high-efficiency energy conversion, well-matched thermal reflectance, and environmental friendliness of our polymer wastewater collector, we anticipate that our strategy of solar water evaporation is very promising towards the industrial application of desalination and water purification.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2021.131199>.

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