

A Low-Cost and Reusable Photothermal Membrane for Solar-Light Induced Anti-Bacterial Regulation

*Qianhao Pan, Shiming Zhang, Ruiting Li, Yonglin He, Yapei Wang**

Department of Chemistry, Renmin University of China, Beijing 100872, China

1. Supplementary Methods

Materials and Characterizations

Glass fiber membranes were purchased from Shanghai Yiming Filtration Technology Co., Ltd. Pyrrole was provided by Shanghai Zane Energy Chemical Co., Ltd. Ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) was obtained from Beijing LYN Technology Co., Ltd. Nutrient agar and nutrient broth (NB) were purchased from Beijing Aoboxing Bio-tech Co., Ltd. Optical images of pristine membranes and a series of polypyrrole-modified membranes were recorded on a digital camera (Canon EOS 70D). Porous structures of membranes were characterized by a scanning electron microscope (SEM, JEOL-6700). Porosity of the membranes was evaluated on a mercury-injection apparatus (AutoPore IV 9500). UV-Vis-NIR spectrophotometer was used to acquire the reflection spectra of these membranes (Shimadzu UV-3600 PLUS). The solar simulator (Solarbeam-02-3A) was supplied from CROWNTECH, INC. And an infrared camera (Fluke Tix 660) was used to detect the surface temperature of these membranes and capture the infrared images. CFU number was obtained by a colony counter (Shineso icount30).

Preparation of Anti-Bacterial Photothermal Membranes

The anti-bacterial photothermal membranes were prepared by a two-step method. Typically, the pristine membrane was cut into 2 x 2 cm² square slices and soaked in a $(\text{NH}_4)_2\text{S}_2\text{O}_8$ aqueous solution (0.1 M) for 5 min. Then, the cover fixed with wetted membrane was hang above the container loaded with 10 mL pyrrole for 5 minutes, and polypyrrole was formed in-situ once the wetted membrane was encountered with pyrrole vapor. The modified membranes were rinsed with deionized water and

ethanol repeatedly to remove excessive oxidant and unreacted pyrrole. Modified membranes with deep black color were obtained for subsequent use after drying in a vacuum oven for 5 min.

Photothermal Conversion Tests under Solar Light

The photothermal conversion efficiency (η_{PT}) can be calculated according to our previous work.^{1,2}

In a representative test process, the pristine and polypyrrole-modified membranes were fixed under a solar light simulator. Illumination time was set as 5 min on the simulator and a circular Fresnel lens was utilized to adjust the light power density. An infrared camera was used to monitor real-time temperature change on the membrane surface.

The efficiency is easily obtained and the photothermal efficiency of polypyrrole-modified membrane made from 0.1M oxidant is 21.4% when the laser power is one sun (AM 1.5). Detailed figures are shown as follow.

Photothermal area test

Different power density of the sunlight emitted from the solar simulator could be strengthened by adjusting the distance between the membrane and the lens. 4.5 sun was set as sunlight supplier in consideration of ample power density and satisfactory illumination area. Typically, a 15 x 15 cm² square polypyrrole-modified membrane (0.1M) was selected as the test membrane. The initial temperature was set as 15°C by symmetrically evaporating ethanol from the membrane surface shown as black area in the infrared images. After solar illumination for 3 seconds, the temperature

of the irradiated areas increased dramatically, and correspondingly, the area was turned into pink and bright white color as observed by the IR camera, representing the effective photothermal conversion.

Anti-Bacterial Ability Test of the Membranes

The anti-bacterial ability of membranes was presented by bacterial CFU. In consideration of infectivity and existence universality, we chose *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) on behalf of gram-negative and gram-positive bacteria, respectively, to investigate the antibacterial performance based on photothermal conversion. At first, *E. coli* and *S. aureus* were cultivated in nutritious broth. 0.5 mL of the suspension was sprayed onto the membrane surface and the membrane was immediately put under the solar simulator to accept 1 min solar illumination. Then, the membrane was cut into pieces and embedded into a test tube containing 10 mL phosphoric acid buffer (PBS) solution. A vortex mixer was used to detach bacteria completely from the membrane to obtain bacterial suspension. This suspension was gradually diluted by a factor from 10^2 to 10^{10} and added on the surface of NB solid medium in order (0.5 mL). After incubated at 37°C for 24 h, bacterial colony could be formed and the number could be obtained by a colony counter.

Ultrasound Treatment of the Photothermal Membranes

To prove that the remaining polypyrrole particles have strong adhesion on the glass-fiber surface, the polypyrrole-modified membrane was subjected to ultrasound treatment. Typically, the polypyrrole-modified membrane (0.1 M) was rinsed in

water to receive a 30 min ultrasound treatment. Gravimetric analysis, time-dependent temperature curve and cross-section SEM images of the polypyrrole-modified and pristine membranes were investigated.

Practical Application of Photothermal Membranes

To simulate the practical conditions as air-conditioner filters, insights were provided into the dust-deposition experiments. Dust originating from air conditioner blades was suspended in ethanol solution and then was uniformly spread onto the polypyrrole-modified membranes. The survived bacteria concentration on the dust-deposited membrane was calculated as the method mentioned above. More than this, a device was set up to further identify the membrane practical performance of light-irradiated sterilization. Two methods were used to produce air-flowing conditions. In the first one, the *E. coli* inoculum was loaded into the device through a window in the middle. By elevating the current of the fan, the suspension was blown out and received by the membrane fixed on the top. In the second one, the *E. coli* inoculum was directly added on the polypyrrole-modified membrane fixed on the top with a spray bottle. The survived bacteria concentration on the membrane was also calculated as mentioned above.

2. Supplementary Figures

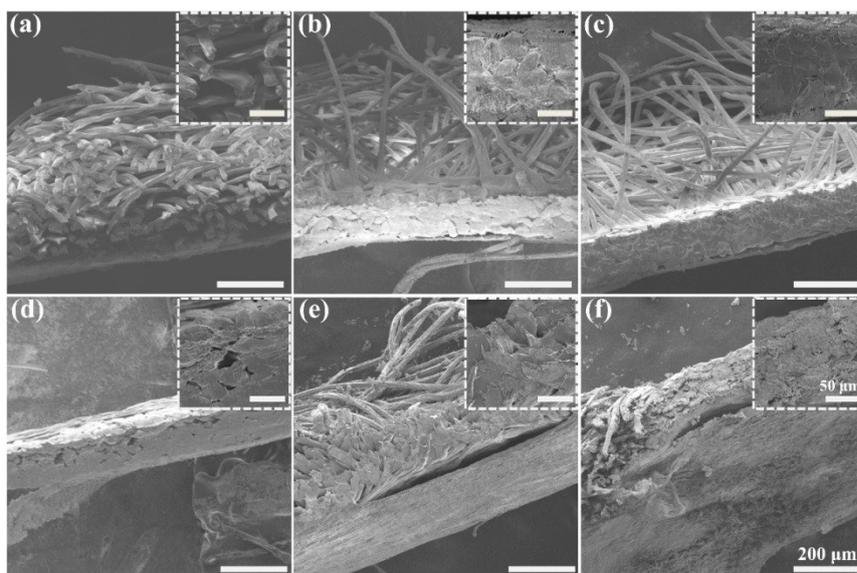


Figure S1. The cross-section images of the glass fiber membranes grown with polypyrrole in the presence of different oxidant concentration: (a) 0 M, (b) 0.01 M, (c) 0.03 M, (d) 0.1 M, (e) 0.2 M, (f) 0.3 M, respectively. Polypyrrole has grown through the membrane when the oxidant concentration is above 0.1 M.

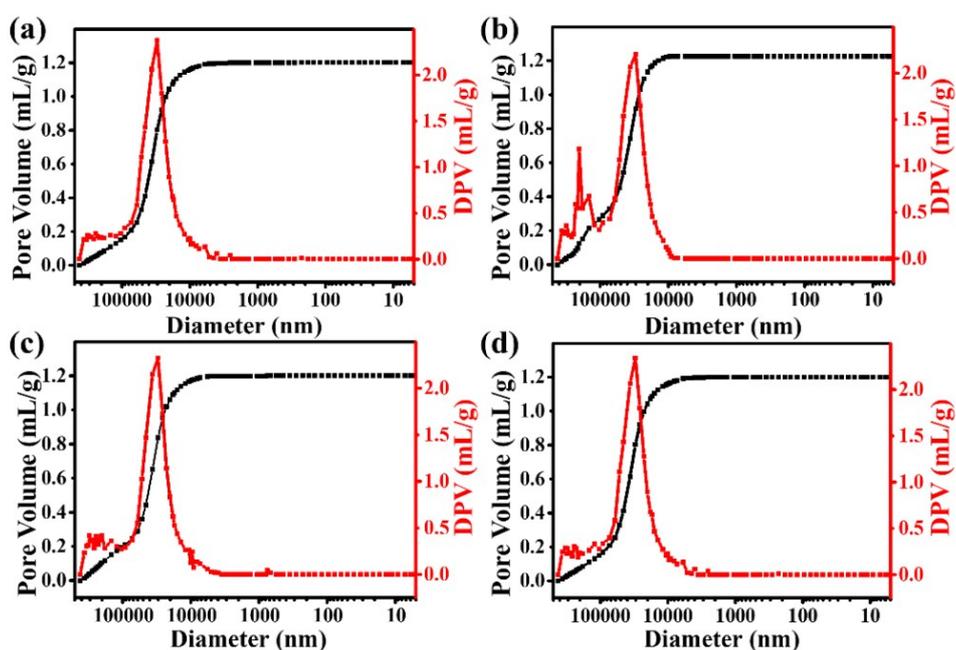


Figure S2. The porosity analysis and specific pore diameter results of polypyrrole-modified membranes with different oxidant concentration: (a) 0 M, (b) 0.1 M, (c) 0.2 M and (d) 0.3 M.

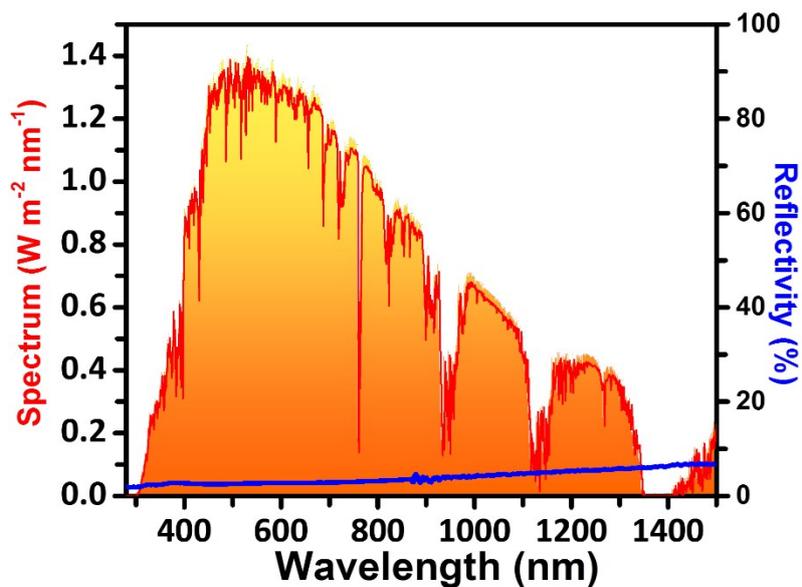


Figure S3. The red line and blue line represent spectrum of AM 1.5 solar light and reflectivity of polypyrrole-modified membrane made from 0.1M oxidant, respectively.

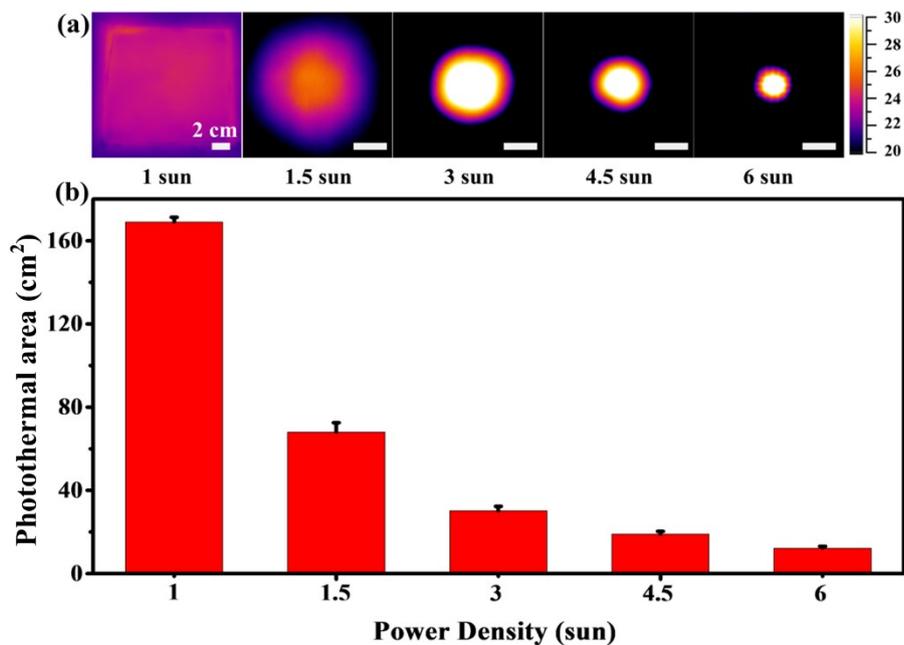


Figure S4. (a) Infrared images of the polypyrrole-modified membrane made from

0.1M oxidant under solar illumination with different power. (b) The relationship between power density and photothermal areas.

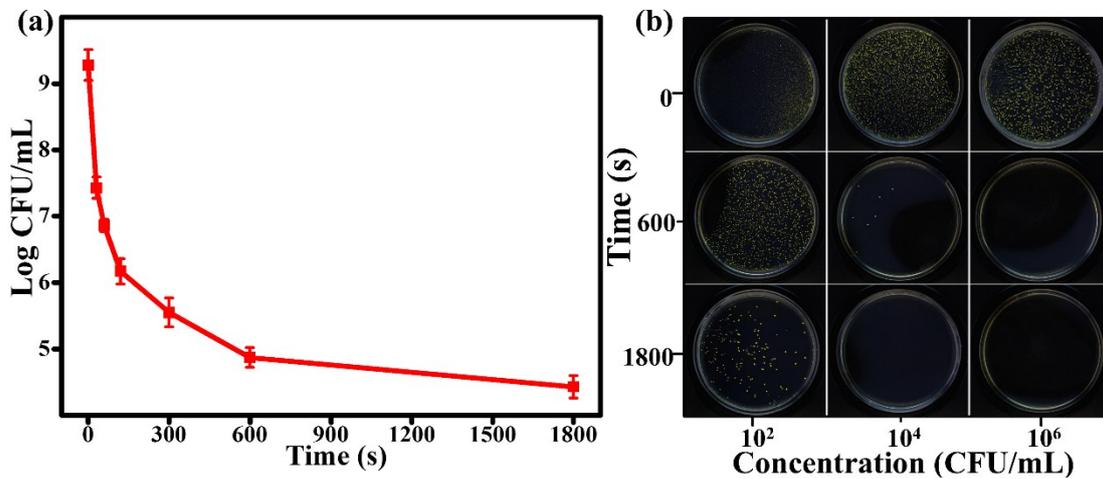


Figure S5. Anti-bacterial tests of the *S. aureus*. (a) Optical images of the bacteria colonies cultured from the polypyrrole-modified membrane (0.1M) under solar illumination. (b) Anti-bacterial results as presented by lg (CFU). The bacteria concentration dramatically decreases from 9.28 lg CFU/mL to 4.43 lg CFU/mL under 1800 s illumination of solar light (power density, 4.5 sun).

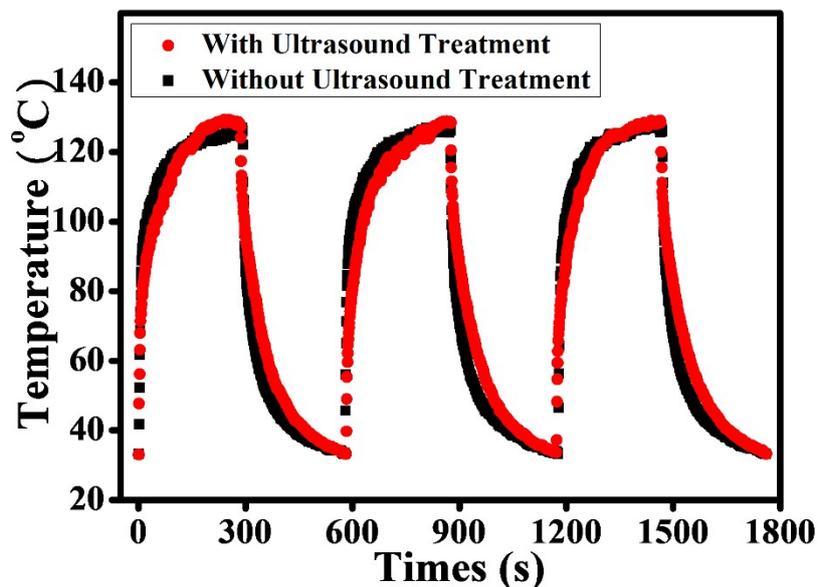


Figure S6. The time-dependent temperature changes of the ultrasound treated and untreated polypyrrole-modified membrane (0.1M). The solar power density is set as

4.5 sun.

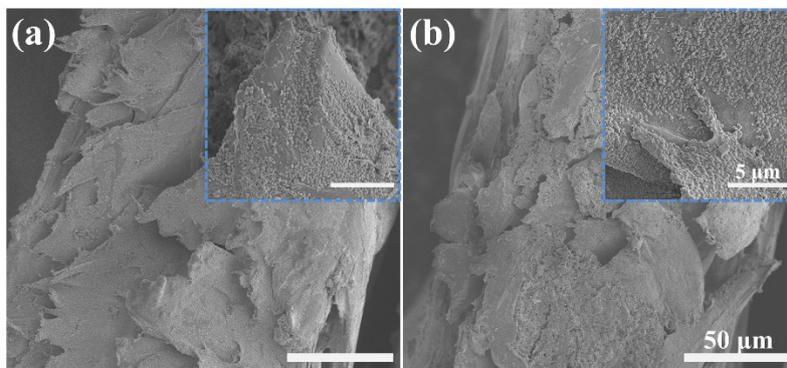


Figure S7. The cross-section SEM images of the (a) ultrasound treated and (b) untreated polypyrrole-modified membrane (0.1M).

Table S1. Gravimetric analysis of the polypyrrole-modified membranes

Concentration (mol/L)	Pristine Mass (mg)	Modified Mass (mg)	Mass Increment Percentage (%)
0.01	31.15	31.40	0.80
0.03	30.15	30.57	1.39
0.10	29.35	29.94	2.01
0.20	31.35	32.01	2.11
0.30	29.40	30.05	2.21

Table S2. Gravimetric analysis of the ultrasound treated membranes

Sample Number	Before Ultrasound Treatment (mg)	After Ultrasound Treatment (mg)	Mass Decrement Percentage (%)
1	77.67	77.62	0.064

2	75.75	75.73	0.026
3	88.92	88.89	0.034
4	86.92	86.90	0.023
5	81.01	80.98	0.037
6	73.74	73.70	0.054

2. References for the Supporting Information

1. Y. Y. Cao, J. H. Dou, N. J. Zhao, S. M. Zhang, Y. Q. Zheng, J. P. Zhang, J. Y. Wang, J. Pei, Y. P. Wang, *Chem. Mater.*, 2017, **29**, 718-725.
2. R. T. Li, Z. Wang, P. Han, Y. L. He, X. H. Zhang, Y. P. Wang, *Chem. Eur. J.*, 2017, **23**, 17889-17893.