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Supporting Information

Preparation of hollow tubular TpBD COF and pod-like ZIF-8/H-TpBD COF tubes using porous anodic aluminum oxide membrane as template

Jiayuan He[a†], Rijian Mo[b,c†], Guangzheng Jiang[a], Lei He[c], Chunxia Zhou[a,b], Zhong-Ji Qian[b,c], Pengzhi Hong[a,b*], Chengyong Li[b,c*]

a. College of Food Science and Technology, Guangdong Ocean University, Zhanjiang 524088, China.
b. Shenzhen Institute of Guangdong Ocean University, Shenzhen, Guangdong 518114, China.
c. School of Chemistry and Environment, Guangdong Ocean University, Zhanjiang 524088, China
† These authors have contributed equally to this work and share first authorship.
* Corresponding Author: Pengzhi Hong and Chengyong Li: hongpz@gdou.edu.cn; cyli@gdou.edu.cn

Contents List

Section S1. Experimental materials

1,3,5-Triformylphloroglucinol (Tp) was bought from Tokyo Chemical Industry and was prepared as a solution using chloroform. Benzidine (BD) was provided by Shanghai Aladdin Bio-Chem Technology Co., Ltd. and was prepared as a solution using chloroform. 2-methylimidazole and tetracycline was obtained from Shanghai Macklin Biochemical Co., Ltd. Other reagents, such as zinc nitrate, chloroform, acetone, and phosphoric acid, were purchased from Zhanjiang Kecheng Trading Co., Ltd. Unless otherwise specified, the solution used was prepared using ultrapure water.[1]

Section S2. Experimental equipment

After sputtering the gold thin layer, the morphologies of TpBD COF nanotubes and the cross-sectional morphologies of the prepared TpBD/AAO were investigated by scanning electron microscope (SEM, Hitachi S-4800) at the accelerating voltage of 5 kV. The samples for cross-sectional examinations were obtained by fracturing the nonwoven-free PAN layer in liquid nitrogen. Transmission electron microscope (TEM) images of TpBD nanotubes were observed by JEOL-100CXII microscope (JEOL, Japan). Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) of TpBD/AAO and AAO was collected by a Nicolet IS50 spectrometer (Thermo Scientific, USA) with pure KBr as background. The XRD patterns were obtained from D/max-2500 diffractometer (Rigaku, Japan) using CuKa radiation (λ=1.5418 Å) with a scan speed of 5° min-1 and 2θ range of 0.5-90°. N_2 sorption isotherms of the obtained samples were measured by a Quantachrome Autosorbe-1 analyzer at 77 K. The surface area and porosity of the obtained samples were analyzed by Brunauer-Emmet-Teller (BET)[2, 3]. The absorbance value was determined by UV-V (U-3900H, HITACHI) at 357 nm.

Section S3. Synthesis of H-TpBD COF nanotubes and ZIF-8/TpBD COF peapod composite.

TpBD COF nanotubes were prepared using the AAO as a template. Briefly, AAO membrane was prepared according to the literature[1] and sandwiched in a self-made two-half electrolytic cell with a hole diameter of 10 mm. The two-half electrolytic cell has a hole about 3 mm in the middle to allow the reaction liquid to circulate with each other. Then, 20 mL of Tp (5 mM) and benzidine (BD, 27 mM) were dissolved in 20 mL of chloroform to enhance dissolution,[2] respectively. Next, the prepared Tp and BD solutions were added to the two electrolytic cells of the self-made two-half electrolytic cell and reacted for 7 h to prepare TpBD COF/AAO membrane. Finally, the AAO template was dissolved in 5 M NaOH solution to obtain free-standing H-TpBD COF nanotubes (Scheme 1a).

Similarly, TpBD COF/AAO was sandwiched in a self-made two-half electrolytic cell. Subsequently, 20 mL of zinc nitrate solution methanol solution (49 mM) and 20 mL of 2-methylimidazole methanol solution (39.5 mM) were added to the left and right cells of the two semi-electrolytic cells, respectively. After sealing reaction for 8 h, the solution was taken out, and the electrolytic cell was washed with absolute ethanol (Scheme 1b). Finally, the pod-like structure of the ZIF-8/TpBD COF tube can be obtained by treatment with 20 μL of 1% hydrofluoric acid for 30 seconds and ultrasonication to remove AAO.

Section S4. SEM images of TpBD COF/AAO membrane synthesized by Tp and BD under different reaction times.

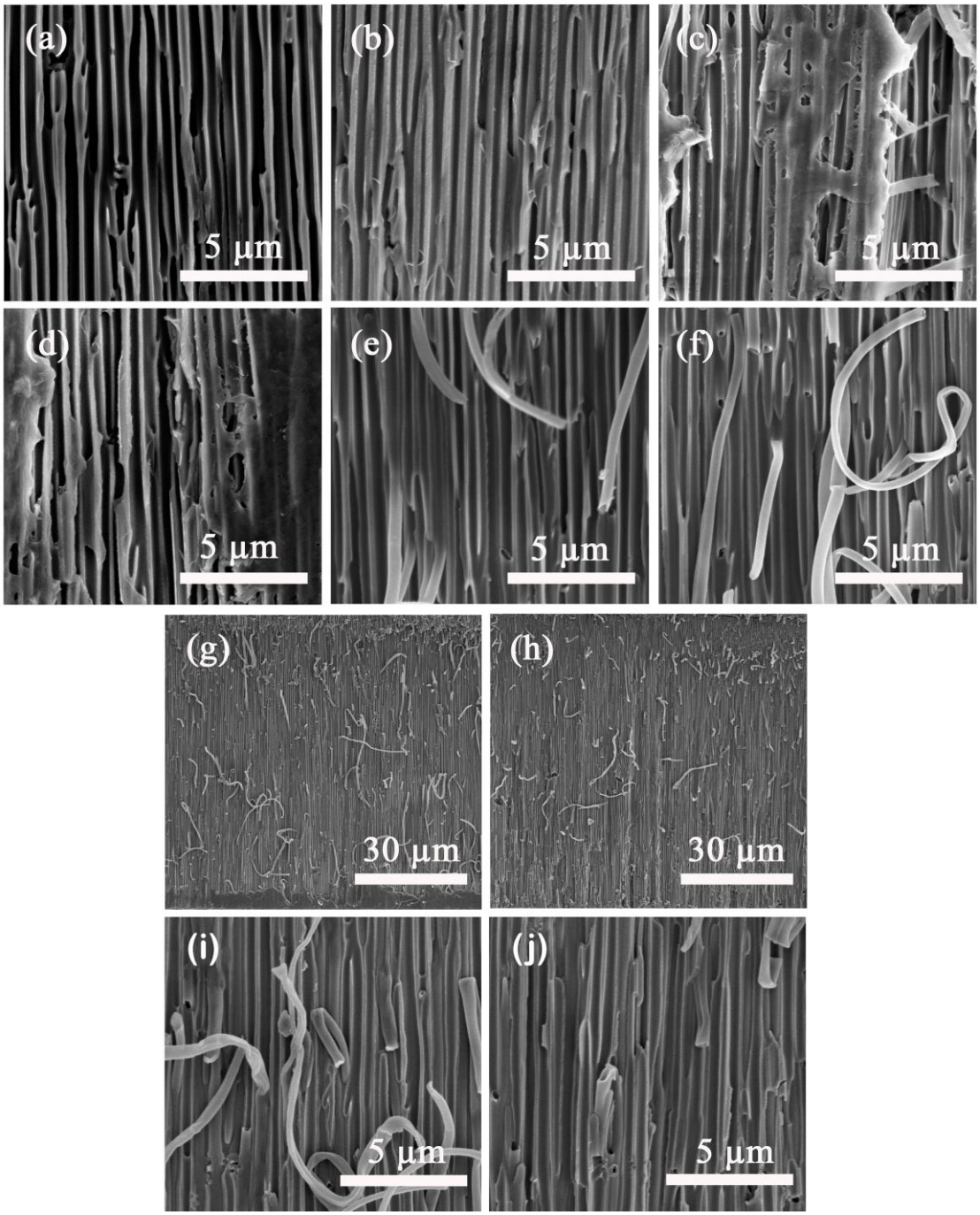

Figure S1 SEM images of TpBD COF/AAO membrane synthesized by Tp and BD under different reaction times. (a) 1 h. (b) 2 h. (c) 3 h. (d) 4 h. (e) 5 h. (f) 6 h. (g) and (i) 7 h. (h) and (j) 8 h.

Section S5 SEM images of AAO membrane and TpBD COF tubes

Figure S2 (a)The diameter of TpBD COF/AAO tubes; (b) The structure of COF tubes by removal AAO membrane in 0.1 M NaOH solution; (c) SEM images of AAO membrane.

Section S6. The diameter distribution diagram of TpBD COF tubes.

The COF tubes starts to form when the reaction time is 5 hours, so this figure calculates the diameter of the tubes generated after 5 to 8 hours. The distribution diagram of the inner and outer diameters of the tube in Figure S3 and S4, with the inner diameter of 160 nm and outer diameter of 211 nm.

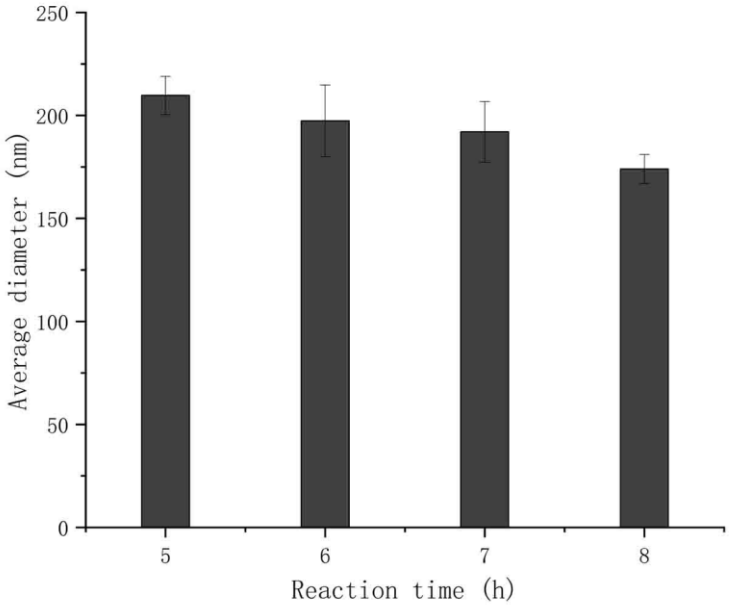

Figure S3 The diameter distribution diagram of TpBD COF tubes.

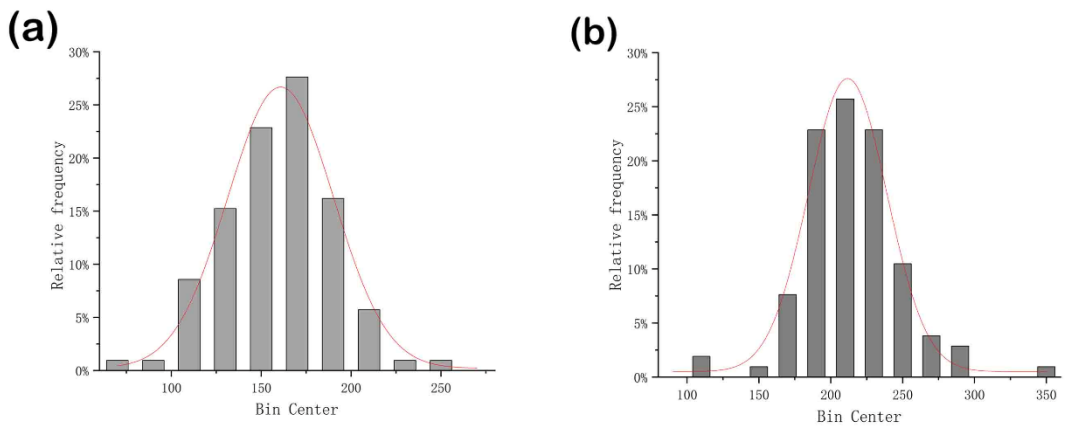

Figure S4 Distribution diagram of the (a) inner and (b) outer diameters of the H-TpBD COF tube.

Section S7. Tetracycline adsorption

The 1 mg of H-TpBD COF and ZIF-8 @H-TpBD COF were dissolved in tap water with 50 μL of tetracycline standard solution (0.1 mg/mL), and the final volume was 1 mL. The content of residual tetracycline in the supernatant was determined after adsorption for 1 hour. The ratio of the content of tetracycline to the total content is calculated as the adsorption rate.

Section S8. References

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