## **Supporting Information**

# Superpermeable Nanoporous Carbon-Based Catalytic Membranes for Electro-Fenton Driven High-Efficiency Water Treatment

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#### 1. Experimental

#### 1.1 Preparation of 2D ZIF-8.

A methanolic solution (500 mL) of zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, 7.4350 g, 25 mmol) was added into a methanolic solution (500 mL) of 2-methylimidazole (2.0520 g, 25 mmol) and triethylamine (3.2675 g, 36 mmol). And then the 3-dimensional (3D) ZIF–8 was exfoliated with ultrasonication for 30 min at ambient temperature to obtain the ultrathin 2-dimensional (2D) nanosheets, giving a turbid flocculent solution. The turbid flocculent solution was allowed to stand for 4 h and then centrifuged to give a white solid, which was washed for five times with methanol and then dried at 80 °C for 4 h to afford ultrathin 2D ZIF–8.

#### 1.2 Preparation of functionalized nanoporous carbon.

2D ZIF–8 samples (4.0 g) were transferred into a ceramic boat and placed into a temperature-programmed furnace under H<sub>2</sub> flow, heated from room temperature to 1000 °C in 3 h, and then kept at 1000 °C for 10 h and cooled down to room temperature. The resultant black material was washed several times with a HCl (5 vol% in water) solution, followed by washing with plenty of distilled water and dried at 80 °C for 12 h to afford 2D ZIF–8-derived hierarchically nanoporous carbon, denoted as PC. Subsequently, the functionalized PC was fabricated by a surface oxidation in 1.0 M acidic ammonia persulfate solution at 100 °C for 12 h to obtain the functionalized carbon matrix. The surface-functionalized PC was recovered by filtration, followed by being washed with water until pH of the filtrate was nearly neutral. Excessively washed surface functionalized PC was collected by the freeze drying for 24 h,

and stored at room temperature, named as TPC. The abundant carboxyl groups on the TPC surface increases the surface hydrophilicity for enhancing their miscibility in aqueous solution.

Surface pore sizes of TPC nanosheets were regulated with  $H_2O_2$  in hydrothermal process. Typically, a 1 mL diluted  $H_2O_2$  aqueous solution (3%  $H_2O_2$ ) was added into 10 mL 2 mg•mL<sup>-1</sup> TPC aqueous dispersion in a 25 mL Teflonlined autoclave. The mixture was sealed and heated at 180 °C for 6 h and naturally cooled down to room temperature, denoted as TPC<sub>2</sub>. In control experiments, 0.3% (TPC<sub>1</sub>) and 30% (TPC<sub>3</sub>)  $H_2O_2$  aqueous solution of the same volume (1 mL) were used to investigate the effect of  $H_2O_2$  concentration on the chemical etching of TPC nanosheets.

#### **1.3 Membrane performance tests.**

The water flux J (L•m<sup>-2</sup>•h<sup>-1</sup>•bar<sup>-1</sup>) was measured by collecting the permeate water (V) through the membrane using an electronic balance and calculated using the following equation:

$$J = \frac{V}{A \times t \times P} \tag{1}$$

Where V is the water volume penetrating the membrane in a certain time t, A is the total effective area of the membrane and P is the pressure.

#### 1.4 H<sub>2</sub>O<sub>2</sub> analytical methods.

The  $H_2O_2$  concentration was determined by flow-injection chemiluminescence method.<sup>[1]</sup> Typically, 0.65 mM of luminol solution was composed of 0.1 M of Na<sub>2</sub>CO<sub>3</sub> (adjusting pH to 10.15 using 2 M of HCl and placing for 24 h), and then CoCl<sub>2</sub> (0.06 mM of Co<sup>2+</sup>) was added into above solution. The luminol solution and sample were injected in chemiluminescence system (MIP–B) simultaneously through the flow injection apparatus (IFISD). Finally, the chemiluminescent signal was recorded to determine  $H_2O_2$  concentration.

#### 1.5 Synthesis of 5, 10, and 25 nm AuNPs.

The 5 nm AuNPs were prepared by the sodium borohydride reduction method described elsewhere.<sup>[2]</sup> The 10 nm and 25 nm AuNPs were prepared using sodium citrate as reducing.<sup>[3,4]</sup> These AuNPs were used for filtration directly without any post-treatments.

#### 1.6 Energy consumption.

Energy consumption is one of the major concerns for membrane separation technology in practical applications. According to Schäfer et al., the energy cost for microfiltration is approximately 30 Wh•m<sup>-3</sup> for the removal of natural organic matter  $(5-12.5 \text{ mg} \cdot \text{L}^{-1})$  from surface water.<sup>[5]</sup> For the case of electro-assisted filtration, on the one hand, the permeate flux of the TPC&Fe membrane was increased by ~80% relative to that without electro-assistance at biases of –0.6 V. On the other hand, the electro-assisted process could cause additional energy consumption of around <1 Wh/m<sup>3</sup> at –0.6 V based on our measurement. Considering the energy savings owing to the increased flux under electro-assistance, the energy cost for the integrated process is less than that for the conventional process, indicating that the process is energy-efficient.

## 2. Results and Discussion



Figure S1. FT-IR spectra of TPC, an obvious band is shown at 1720 cm<sup>-1</sup> after wet oxidation

assigned to the stretching vibration of carboxylic groups.



Figure S2. A photograph of vacuum filtration system.



Figure S3. TEM images of functionalized PC etched using (a) 0.3%, (b) 30% and (c) 3% of  $H_2O_2$ .

Sample	BET $(m^2 \cdot g^{-1})$
Non-etched TPC	~300
TPC&Fe membrane	~2100

 $\label{eq:solution} \textbf{Table S1.} \ N_2 \ \text{sorption isotherms of TPC} \& Fe \ \text{membrane and non-etched TPC}.$ 



Figure S4. Raman spectra of PC,  $TPC_1$  (etched by 0.3%  $H_2O_2$ ),  $TPC_2$  (etched by 3%  $H_2O_2$ ) and

TPC<sub>3</sub> (etched by 30% H<sub>2</sub>O<sub>2</sub>).



Figure S5.  $H_2O_2$  production rates (-0.6 V, pH 3) of PC, TPC<sub>1</sub> (etched by 0.3%  $H_2O_2$ ), TPC<sub>2</sub>

(etched by 3%  $\rm H_2O_2)$  and TPC3 (etched by 30%  $\rm H_2O_2).$ 



Figure S6. The C 1s XPS spectrum of (a) TPC and (b) PC.



Figure S7. Digital photos of PC and TPC placed in room for a week. It can be seen that the TPC

materials have strong hydrophilicity compared with PC under the same condition.

Membrane	Water contact angle (°)	References	
PVDF membrane	79	6	
Al <sub>2</sub> O <sub>3</sub> ceramic membrane	75	6	
Polycarbonate membrane	77	6	
CNTs/Al <sub>2</sub> O <sub>3</sub> membrane	72	7	
Carbon nanotube-based ultrathin membrane	56	8	
TPC&Fe membrane	45	This work	

 Table S2. Comparison of water contact angle for different membranes.



Figure S8. Cross-section SEM image of TPC&Fe membrane. Inset in Figure S8: A magnified

SEM image of TPC&Fe membrane.



**Figure S9.** High-resolution scanning XPS spectra for Fe 2p regions of TPC&Fe membrane (a)

before reaction and (b) during the reaction.

The surface chemical information on TPC&Fe membrane was further explored by XPS survey. The wide-scan XPS spectra represented in Figure 2f reveals that both as-synthesized samples are only composed of C, O, N and Fe elements. The highresolution Fe 2p spectra of TPC&Fe membrane before reaction and during the reaction was illustrated in Figure S9. For the TPC&Fe membrane, the typical peaks of Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  were mainly centered at around 711.4 and 724.8 eV, respectively, which could both be deconvoluted into two components. Thereinto, the fitted peaks at 711.3, 713.9, 724.8, and 727.3 eV are normally assigned to the Fe<sup>3+</sup> cation, and the two shakeup satellite peaks located at 717.8 and731.7 eV are the fingerprint of Fe<sup>3+</sup> species, which indicate that the iron in TPC&Fe membrane is predominantly in the Fe<sup>3+</sup> state.<sup>[9,10]</sup> However, new multiplet peaks at 709.6 and 723.1 eV, which are attributable to the characteristics of Fe<sup>2+</sup>, appeared in the deconvoluted curves of Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  of TPC&Fe membrane during the reaction with electroassistance.<sup>[11,12]</sup> This infers that some Fe<sup>3+</sup> centers of TPC&Fe membrane undergo a valence variation to generate  $Fe^{2+}$  in the presence of electro-assistance.



Figure S10. Phenol removal over TPC&Fe membrane with electro-assistance as a function of Fe<sup>3+</sup>

loading (pH 3).



**Figure S11.** (a) Cycling runs for phenol removal with TPC&Fe membrane under electroassistance; (b) SEM image of TPC&Fe membrane after the 5<sup>th</sup> electro-assisted filtration cycle.

A cyclic coinstantaneous filtration and electro-Fenton process was performed to estimate the stability and reusability of the prepared membranes. As shown in Figure S11a, the TPC&Fe membranes maintain high separation performance (> 90%) during five cycles. These results indicate that the TPC&Fe membrane possesses excellent stability during long-term operation which can be attributed to efficient •OH radical scavenging activity. The SEM image in Figure S11b depicts a stable and unbroken TPC&Fe membrane structure even after the 5<sup>th</sup> electro-assisted filtration cycle.

Membrane	Water flux (L•m <sup>-2</sup> •h <sup>-1</sup> •bar <sup>-1</sup> )	Removal rate (%)	Pollutant type	Applied voltage (V)	References
PVDF-SO₃H	~2500	96.9	Methyl orange	-0.8	13
			(0.1 mM)		
CNTs/Al <sub>2</sub> O <sub>3</sub> membrane	~860	99.3	Phenol	1.5	7
			$(5 \text{ mg} \cdot \text{L}^{-1})$		
CNTs-HFMs	~2200	56.8	Sodium alginate	-1.2	14
			(1g•L <sup>-1</sup> )		
TPC&Fe membrane	~8000	97.4	Bisphenol A	-0.6	This work
			(5 mg•L <sup>-1</sup> )		

**Table S3.** Comparison of membrane performance for different membranes.

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