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# <sup>1</sup> Electrospun flexible self-standing Cu-Al<sub>2</sub>O<sub>3</sub> fibrous membranes as

## 2 Fenton catalysts for bisphenol A degradation

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Abstract: Novel flexible self-standing Cu-Al<sub>2</sub>O<sub>3</sub> fibrous membranes have been successfully 9 synthesized via electrospinning technique, which exhibited high Fenton catalytic activities under 10 neutral pH values. The copper species distribute uniformly in the fibers with the form of  $Cu^+$  and 11 Cu<sup>2+</sup>, which was responsible for the Fenton catalytic performance. Over 87% BPA was degraded 12 within 180 min in the membrane reactor using the 1 wt% Cu-Al<sub>2</sub>O<sub>3</sub> membrane in neutral pH values 13 with  $H_2O_2$  addition. The membranes can continuously degrade BPA by batch in the membrane 14 reactor without any other extra separation process. The excellent catalytic performance, good 15 flexibility of the membranes, as well as the facile preparation process supposed the membranes to be 16 17 good candidates as novel heterogeneous Fenton catalysts.

18 Keywords: Electrospinning; Cu-Al<sub>2</sub>O<sub>3</sub> fibrous membranes; Fenton catalysts

### 1 **1. Introduction**

Recalcitrant organic pollutants are frequently detected in the water environment and being a 2 serious health hazard to mankind.<sup>1,2</sup> Developing an effective and practical method to remove the 3 organic pollutants is of significance and becoming a research hotspot these years.<sup>3,4</sup> Fenton processes 4 are efficient advanced oxidation processes (AOPs) to remove organic pollutants from water.<sup>5</sup> In 5 Fenton reaction, highly aggressive free hydroxyl radicals (•OH) were generated via the reduction of 6 hydrogen peroxide  $(H_2O_2)$  with Fe<sup>2+</sup> or other reducing transition metals.<sup>6</sup> It is well known that there 7 are two main limitations for the homogeneous Fenton process, which includes the low pH value 8 range (3-5) required in the reaction as well as the iron containing sludge accumulation.<sup>7, 8, 9</sup> As 9 alternatives, the heterogeneous Fenton catalysts could minimize the above disadvantages, and 10 various kinds of heterogeneous catalysts including supported gold nanoparticles,<sup>5</sup> iron-containing 11 solids,<sup>9, 10, 11</sup> and bimetallic composites,<sup>12</sup> have been developed. However, mostly, the pH values of 12 the solution still need to be adjusted to 3~5, and more efforts are needed for exploring Fenton 13 catalysts with high catalytic performance at neutral pH values. 14

15 Cu-based materials exhibit a Fenton catalytic activity with a wide pH range from 3 to 7. Up to now, 16 various Cu-based Fenton catalysts such as Cu doped mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\gamma$ -Cu-Al2O3),<sup>13</sup> copper– 17 aluminum–silica nanospheres,<sup>14</sup> and Cu-containing zeolites,<sup>15</sup> have been developed. Nevertheless, up 18 to now, the Cu-based heterogeneous Fenton catalysts are scattered forms in macrograph, which 19 usually disperse in water, and need filtration or centrifugation to separate them after use. Sometimes 20 the incomplete separation will lead to a possible catalyst lost and a second pollution to water.

Electrospun fibrous membranes are composed of nanofibers with small diameter, and many 21 interconnected open pores existing in the membranes. Thus the membranes possess good 22 permeability and are favored in many environmental remediation areas.<sup>16,17</sup> Meanwhile. 23 electrospinning technique offers a simple and versatile way to fabricate nanofibers, membranes and 24 films from various materials.<sup>18,19,20</sup> However, most inorganic membranes are fragile and transform to 25 scattered form during use. Up to now, only a few kinds of flexible inorganic membranes have been 26 developed via electrospinning method, such as SiO<sub>2</sub>-TiO<sub>2</sub> composite membranes,<sup>17</sup> 27 silica/mesoporous alumina core-shell fibrous membranes<sup>21</sup> and  $\gamma$ -alumina fibrous membranes.<sup>22</sup> 28 Most of these membranes are limited to adsorption or filtration performance. The membranes with 29

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catalytic performance are still needed more efforts to study. Therefore, the research on fabricating
 membranes with a high Fenton catalytic activity is desired.

Herein, a novel flexible self-standing Cu-Al<sub>2</sub>O<sub>3</sub> fibrous membrane was fabricated via electrospinning technique. The Cu-Al<sub>2</sub>O<sub>3</sub> membrane was composed of randomly arranged nanofibers, and the copper species distribute uniformly in the fibers. The high Fenton catalytic activities of the membranes were exhibited, which suggested that the Cu-Al<sub>2</sub>O<sub>3</sub> fibrous membranes are good candidates as Fenton catalysts.

### 8 2. Experimental section

### 9 **2.1 Preparation procedure**

10 All materials were analytical grade and commercially purchased without any further purification, 11 including HCOOH, CH<sub>3</sub>COOH, aluminum powder, polyethylene oxide (PEO,  $M_W$ =500000), 12 polyvinylpyrrolidone (PVP,  $M_W$ =1300000), CuSO<sub>4</sub>.

**Preparation of alumina sol.** The alumina sol was prepared according to our previous reports with some modifications.<sup>22</sup> In a typical synthesis, 30.16 mL HCOOH and 34.29 mL CH<sub>3</sub>COOH were dissolved in 86.4 mL deionized water. Then, 5.4 g aluminum powder was added to the solution. The mixture was stirred and refluxed at 60-80 °C until the aluminum powder had reacted completely. The solution was filtered to remove a small amount of possible particulates to guarantee the clarity of the solution. Finally, 125 mL colorless transparent alumina solution was obtained.

### 19 Preparation of copper-alumina electrospinning precursor.

10 mL of the alumina sol was taken in to a 25 mL beaker, then 0.035 g PEO and 0.035 g PVP were added and the solution was stirred for 2 h. Then 0.0408 g CuSO<sub>4</sub> was added and stirred for 1 h to prepare the to prepare electrospinning precursor for the Cu-Al<sub>2</sub>O<sub>3</sub> fibrous membrane with 1wt% copper content, which denoted as 1 wt% Cu-Al<sub>2</sub>O<sub>3</sub>. Similarly, 0.1224, 0.204 and 0.2856 g CuSO<sub>4</sub> were respectively added to the 10 mL solution to prepare electrospinning precursor for the 3 wt%, 5 wt%, 7 wt% Cu-Al<sub>2</sub>O<sub>3</sub> fibrous membrane.

### 26 Preparation of Cu-Al<sub>2</sub>O<sub>3</sub> fibrous membrane

The electrospining process was performed on a SS-2535H device (Ucalery Inc., Beijing, China.) with the parameters as follows: The volume of the plastic syringe was 10.0 mL, the inner diameter of the electrospinning metallic needle was 0.9 mm, the push speed was 2.0 mL/h, the distance between

# 1 the needle and the collector was 25.0 cm, the applied voltage was 12 kV, and the humidity was below

2 10%. After electrospinning, the xerogel fibrous membranes are obtained.

The xerogel fibrous membranes were calcined at high temperatures with 1 °C min<sup>-1</sup> heating rate and kept at the target temperature for 2 h. and The membranes calcined at 600, 700 and 800 °C were denoted as Cu-Al<sub>2</sub>O<sub>3</sub>-600, Cu-Al<sub>2</sub>O<sub>3</sub>-700 and Cu-Al<sub>2</sub>O<sub>3</sub>-800, respectively.

### 6 2.2 Characterization

The morphology of the fibers was characterized on a field emission scanning electron microscope 7 (SEM, SU-8020, Hitachi, Japan). Transmission electron microscopy (TEM) was performed by 8 9 H7500 microscope (Hitachi, Japan). X-ray diffraction (XRD) were measured on a X'pert PRO MPD PC system using Cu Kα (λ=0.15 418 nm, 40 kV, 40 mA) as the X-ray source. X-ray photoelectron 10 spectroscopy (XPS) was performed on a Phi Quantern instrument. The binding energy (B. E.) 11 measurements were calibrated for charging effects with C 1s peak (284.8 eV) as the reference. 12 Thermo-gravimetric (TG) and differential scanning calorimetry (DSC) measurements were 13 characterized on a Mettler TGA-1 thermogravimetric analyzer with a heating rate of 10 °C min<sup>-1</sup> and 14 up to 1000 °C in air atmosphere. The diffuse reflectance absorption spectra (DRS) were investigated 15 in the range from 200 to 800 nm on a MAYA 2000 PRO (OCEANOPTICS INC.) spectroscope. N<sub>2</sub> 16 17 adsorption-desorption isotherms were tested on a Quadrasorb SI apparatus. All the membranes were degassed at 200 °C under a vacuum for 5 h before analysis. 18

### **19 2.3 Fenton oxidation experiments**

The Fenton catalytic performance of the Cu-Al<sub>2</sub>O<sub>3</sub> membranes was tested by fixing 10 mg membrane in the membrane reactor. 10 mL BPA aqueous solution (20 mgL<sup>-1</sup>) was added into the reactor, and stirred to establish adsorption/desorption equilibrium. Then, 12 mM H<sub>2</sub>O<sub>2</sub> was added and the solution kept stirring unless otherwise specified. At appropriate time intervals, 0.50 mL solution was collected and mixed with 500  $\mu$ L methanol to quench the residual •OH, and then filtered through a Millipore filter (pore size 0.45  $\mu$ m) for HPLC analysis.

The samples were analyzed using a HPLC (LC-20AT,Shimadzu) equipped with a  $C_{18}$ reversed-phase column (250 mm × 4.6 mm,5 µm, GL, Science Inc.) and a UV detector ( $\lambda = 280$ nm). The mobile phase consisted of a 70/30 v/v mixture ofmethanol/water at a flow rate of 1 mL/min. Total organic carbon (TOC) was determined by a Shimadzu TOC-VCPH analyzer. The leaching copper and aluminum ions from the membranes after catalytic reaction were determined by ICP-OES 1

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(OPTIMA 2000, Perkin Elmer Co., U.S.A.). The electron spin-resonance (ESR) spectra were recorded on a BrukerA 300-10/12 ESR spectrometer at room temperature and DMPO was used as spin trap agents.

The intermediates of BPA degradation were identified by UPLC-Q-TOF-MS (ACQUITY UPLC, Quattro Premier XE, Waters, America) with a C18 column (2.1 mm $\times$ 50 mm $\times$ 1.7 µm). The mobile phase containing A (mili-Q water) and B (methanol) was delivered at 0.3 mL min<sup>-1</sup>. The gradient was 99% A for 15 min, then decreased to 80% for 10 min, then 50% for 10 min, and then increased to 99% for 4 min. The mass spectrometer was operated in the m/z 50-800 range with negative electrospray ionization.

### 10 **3. Results and discussion**

### 11 3.1 Fabrication and morphology of Cu-Al<sub>2</sub>O<sub>3</sub> membranes





Fig. 1. Schematic illustration of the formation of Cu-Al<sub>2</sub>O<sub>3</sub> membrane.

The formation of Cu-Al<sub>2</sub>O<sub>3</sub> fibrous membranes involves several processes. As shown in Fig. 1, 14 15 the alumina powder was reacted with carboxylic acid to acquire a stable homogeneous alumina solution <sup>22</sup>. Then a small amount of PVP and PEO were added to respectively adjust the spinnability 16 and viscosity of the alumina solution, and  $CuSO_4$  was dissolved in the solution. Hence, a light blue 17 transparent electrospinning precursor, which contains evenly distributed Cu<sup>2+</sup> and Al<sup>3+</sup> was formed. 18 19 During the electrospinning process, the solvent evaporate rapidly, leading to the immediately 20 formation of Cu-Al<sub>2</sub>O<sub>3</sub> nanofibers with high aspect ratio. The electrospinning method can avoid the 21 long time evaporation of solvent by the evaporation-induced self-assembly method that involves in 22 most literatures, and can directly obtain the membrane form catalysts. The details of the methods for

preparing Cu-Al<sub>2</sub>O<sub>3</sub> catalysts are discussed in the supporting information. As shown in Fig. S1A, 1 SEM images indicate that the fibers are continuous with high aspect ratios. The average diameter is 2 ca. 500 nm. TG-DSC curves (Fig. S1B) of the xerogel membranes indicate that the mass loss 3 (65.05%) mainly occurred before 500 °C, which was caused by the decomposition of organics as 4 well as the removal of H<sub>2</sub>O. Correspondingly, three exothermic peaks in the range of  $30 \sim 500$  °C are 5 observed in the DSC curves. Hence, the calcination temperatures were chosen above 500 °C. After 6 calcinations, the flexible Cu-Al<sub>2</sub>O<sub>3</sub> membranes were formed, and -Al-O-Cu- chemical bond was 7 supposed to formed in the fibers. 8



Fig. 2 (A) SEM image, (B) STEM image and (C) TEM image of 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600 membranes,
the insert in (A) is an optical image, and insert in (C) is the HRTEM image of the membranes.

12 The morphology and microstructure of the Cu-Al<sub>2</sub>O<sub>3</sub>-600 membranes were presented in Fig. 2. The membranes could be bended many times and still keep integrated without any cracks, 13 14 demonstrating that the membranes possess excellent flexibility. The SEM image shows that the membranes are uniformly and composed of randomly oriented nanofibers. There are many 15 interconnected open pores in the membranes, which is beneficial for the permeability of the 16 membranes. Fig. S2 presents the SEM images of the Cu-Al<sub>2</sub>O<sub>3</sub> membranes with various Cu content 17 and calcined at various temperatures. It can be seen that all the membranes are composed of 18 randomly arranged nanofibers. The average fiber diameters for the membranes calcined at 600 °C are 19 slightly decreased with the increasing of the Cu content, which are 390, 360, 340 and 320 nm for 1, 3, 20 5, 7 wt% Cu-Al<sub>2</sub>O<sub>3</sub> fibrous membranes, respectively (Table S1). Meanwhile, with the increasing 21 calcination temperatures, the average fiber diameters decreased obviously, which are 340, 270, and 22 190 nm for 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub> membranes calcined at 600, 700 and 800 °C (Table S1). STEM images 23 (Fig. 2B) indicate that the fibers are homogeneous without any particles or other phases, indicating 24 that the copper species distribute homogeneously in the fibers instead of forming copper or copper 25

- 1 oxide particles. The surfaces of the fibers are smooth without any cracks, which are beneficial for its
- 2 flexibility. TEM images (Fig. 2C) further demonstrate the homogeneous of the fibers.



Fig. 3 EDS of a single fiber of 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600.

EDS analysis of a single fiber was carried out to identify the element distribution. In Fig. 3, three 5 elements including Al, O and Cu are observed and distributed uniformly. The copper wire mesh was 6 used for preparing the samples for analysis, thus some Cu elements are detected outside the fiber. 7 The homogeneous distribution of copper element is beneficial for its sufficient contact with the target 8 pollutants in water and thus in favor of the catalytic process. Moreover, the EDS spectrum of the 9 membrane was tested to give an overall analysis of of the elements in the fibers. As presented in Fig. 10 11 S3, five elements including Al, O, Cu, S and Au are observed. Among them, Al, O, and Cu are the main elements of the Cu-Al<sub>2</sub>O<sub>3</sub> membranes, Au is derived from the Au spraying pretreatment, which 12 could enhance the conductivity of the Cu-Al<sub>2</sub>O<sub>3</sub> membrane to get a high quality of SEM image. A 13 small amount of S element is also observed between 2-3 kV, and it is due to the incomplete removal 14 of SO<sub>4</sub><sup>2-</sup> that introduced by CuSO<sub>4</sub>. According to previous reports, H<sub>2</sub>SO<sub>4</sub> is often used as common 15 acid-base regulators to control the pH of the solution, because  $SO_4^{2-}$  rarely affects the degradations.<sup>23</sup> 16 Hence, the small amount of residual  $SO_4^{2-}$  in the fibers is considered to have negligible effect on the 17 catalytic performance of the Cu-Al<sub>2</sub>O<sub>3</sub> membranes. Moreover, the concentration of Cu element in the 18 fiber is 6.59 wt% (Table S2), similar but not the same with the calculated concentration (5 wt%) due 19 to the semi-quantitative analysis of the EDS analysis. 20

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Fig. 4 (A) XRD patterns the 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub> membranes calcined at various temperatures and (B)
UV-Vis DRS of individual Al<sub>2</sub>O<sub>3</sub> and 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub> membranes.

XRD (Fig. 4A) analysis was performed to identify the crystal phase of the membranes. As for the 4 xerogel fibrous membranes and the membranes calcined at 600 °C, no peaks but humps are observed 5 6 in the XRD patterns, indicating that the phase are amorphous. While the peaks of  $\gamma$ -alumina (PDF) card number: 50-0741) appear when the membranes calcined at 700 °C, and the crystallinity 7 becomes better when the calcination temperature increased to 800 °C. In addition, it is worth noting 8 9 that no copper and copper-related diffraction peaks appeared for all the samples, indicating that the copper species with the individual crystal phase were not formed. In the UV-Vis spectra (Fig. 4B), no 10 obvious absorptions are observed for individual Al<sub>2</sub>O<sub>3</sub> membranes. While for Cu-Al<sub>2</sub>O<sub>3</sub> membranes 11 calcined at 600 and 800 °C, the absorption peaks at 750 nm were observed and attributed to the 12 electron transitions in Cu<sup>2+</sup> in alumina lattice,<sup>24</sup> which confirmed that the copper species mostly 13 14 incorporated in alumina matrix.



16 Fig. 5 XPS analysis of the 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600 membrane, (A) XPS survey (B) Cu 2p and

<sup>17 (</sup>C) Al 2p spectra.

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The complete information of the surface of the Cu-Al<sub>2</sub>O<sub>3</sub> membranes were identified by the XPS survey spectrum. As shown in Fig. 5A, the peaks of Al, O, Cu, S and C in the XPS survey spectrum of the 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600 membrane are observed. Among them, Al, O, and Cu are the main elements of the membranes: The S element is derived from the residual  $SO_4^{2-}$  in the membrane, and this is consistent with the EDS analysis (Fig. S3); The peak of C element is appeared unavoidably due to the adsorbed  $CO_2$  from air. In addition, the peaks of S element are absence in the XPS survey spectrum of the 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-800 membrane (Fig. S4), indicating that SO<sub>4</sub><sup>2-</sup> is totally removed

The specific chemical environments and oxidation states of the Cu and Al elements were analysed by Cu 2p and Al 2p XPS spectra (Fig. 5B and Fig. 5C). In Cu 2p spectra, the peaks centred at 933.1 eV was corresponding to the reduction state of copper species. The auger kinetic energy at 914.6 eV based on AES measurements confirmed the reduction state of copper was Cu<sup>+</sup>. The peaks assigned to the oxidation state of copper was observed at 935.1 eV, and the shakeup satellite line at 942.8 eV also appeared, confirming the  $Cu^{2+}$  existing. The atomic ratio of  $Cu^{+}$  to  $Cu^{2+}$  was calculated to be 1.63. These results indicate that the copper species were well doped on the surface of the fibers in the form of Cu<sup>+</sup> and Cu<sup>2+</sup>. The XPS spectra of Al 2p was fitted to two peaks centered at 74.2 and 75.3 eV, respectively ascribing to Al–O–Al and Al–O–Cu. Moreover, the concentration of copper species on the fiber' surface was 4.64 wt% based on XPS analysis, a little lower than that theoretically calculated (5.0 wt%), indicating that the copper species were well dispersed in the bulk matrix.<sup>25</sup> According to previous reports,<sup>26</sup> the dispersed copper species in the bulk alumina matrix can introduce oxygen vacancies  $(V_0)$  and other intrinsic defects, which may result in the excess electrons caused by charge compensation. The excess electrons could stimulate the reducing transformation 22 from  $Cu^{2+}$  to  $Cu^{+}$ , and stable the  $Cu^{+}$  by avoiding its oxidization. Moreover, it is worth nothing that, 23 24 the surface copper concentration increased to 7.69 wt% when the calcination temperature increased to 800 °C (Fig. S4), suggesting that some copper species migrated to the fibers' surface due to the 25 rearrangement of Al, O and Cu atoms during crystallization. 26



Fig. 6 N<sub>2</sub> adsorption-desorption isotherms of (A) Cu-Al<sub>2</sub>O<sub>3</sub>-600 membranes with various copper
content, (B) 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub> membranes calcined at various temperatures.

N<sub>2</sub> adsorption-desorption isotherms of the membranes were analyzed to shed some light on the 5 BET surface area of the membranes. In Fig. 6A, All the Cu-Al<sub>2</sub>O<sub>3</sub>-600 membranes with various 6 copper content exhibit the type-III like adsorption isotherms, which corresponds to the adsorption of 7  $N_2$  on nonporous materials.<sup>21</sup> As shown in Table S3, the BET surface areas were 12.33, 9.26, 10.10 8 and 8.11 m<sup>2</sup> g<sup>-1</sup> for the 1 wt%, 3 wt%, 5 wt% and 7 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600 membranes, respectively. 9 These results indicate that the effect of copper content on the surface area of the Cu-Al<sub>2</sub>O<sub>3</sub> 10 membranes is very small. The surface areas of 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub> membranes calcined at various 11 temperatures were also tested. As shown in Fig. 6B, when the calcination temperature increased to 12 700 and 800 °C, the membranes exhibit type-IV like adsorption branches, indicating the existence of 13 mesopores in the fibers.<sup>22, 27</sup> The BET surface areas were 10.10, 40.56, 38.63 m<sup>2</sup> g<sup>-1</sup> for the 5 wt% 14 Cu-Al<sub>2</sub>O<sub>3</sub> membranes calcined at 600, 700 and 800 °C, respectively. The BET surface area increased 15 when the calcination temperature increased from 600 to 700 °C, and then changed very little form 16 700 to 800 °C. The higher surface area could provide more active sites, and increase the contact area 17 of the active sites and the pollutants, hence improve the degradation rate. 18

### **3.2 Catalytic performance of Cu-Al<sub>2</sub>O<sub>3</sub> membranes**

The Fenton-like catalytic performance of the  $Cu-Al_2O_3$  membranes was evaluated by using bisphenol A (BPA) as the target pollutant, which is a representative endocrine disrupter. Especially, a membrane reactor (Fig. 7) was used for the Fenton reactions. The membranes were cut into the round shape to match the reactor, and then fixed in the bottom of the reactor. Prior to the main experiments,

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the reaction was optimized by varying the  $H_2O_2$  dosage due to it is a key factor that influence the 1 Fenton reaction.<sup>13</sup> The detailed analysis is shown Fig. S5 and discussed in the supporting information. 2 The results indicate that 12 mM was the optimal  $H_2O_2$  dosage in this reaction, and 12 mM  $H_2O_2$  was 3 used in all experiments unless otherwise specified. Fig. 8 presents the results of the Fenton catalytic 4 performance toward BPA degradation under various conditions. In Fig. 8A, nearly no removal of 5 BPA was observed with individual  $H_2O_2$  addition. Meanwhile, ~3% BPA was removed due to the 6 adsorption by the individual membranes, and the adsorption equilibrium established within 30 min. 7 Notably, 82% BPA was removed for 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600 membranes using the membrane reactor 8 9 with the addition of H<sub>2</sub>O<sub>2</sub>, while under the same condition, ~84% BPA was removed by stirring the 10 membranes in a beaker and forming the conventional suspension. The difference on the removal ability of the membrane reaction and the suspension form is slight, suggesting that the molecular 11 mass transfer rate in the membrane reactor is still fast and nearly not affect the catalytic process. 12 Moreover, the effects of initial pH on Fenton catalytic performance were investigated. The initial pH 13 values were adjusted by 0.1 M H<sub>2</sub>SO<sub>4</sub>. As shown in Fig. 8B, ~86% BPA was removed within 180 14 min at pH 3, 5 and 7. The neutral pH values are favorable in practical applications, because there is 15 no need to adjust the pH value. Therefore, the pH value of 7 was chosen as the optimal conditions for 16 17 further investigations.

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Fig. 7 (A) Illustration of the membrane reactor, (B) Picture of a 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600 membrane.



Fig. 8 (A) Removal efficiency of BPA with initial pH 7.0 and (B) the influence of initial pH on the performance of 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600 membranes. Conditions:  $[BPA] = 20 \text{ mg/L}, [H_2O_2] = 12 \text{ mM}.$ 

Fig. 9A presents the catalytic performance of Cu-Al<sub>2</sub>O<sub>3</sub>-600 membranes with various Cu content. 4 5 It can been seen that  $\sim 15\%$  BPA was removed for the individual Al<sub>2</sub>O<sub>3</sub>-600 membrane, while 87%, 82%, 84% and 93% BPA were removed respectively for 1, 3, 5 and 7 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600 membranes. 6 The degradation ability of the membranes with 1~7 wt% Cu content are all satisfying. 7 Correspondingly, the TOC removal percentages were 59.8%, 52.1%, 57.8% and 63.20% for 1, 3, 5 8 and 7 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600 membranes, respectively. These TOC removal percentages were much 9 higher than that in previous reports (10~30%) under similar conditions for Fenton catalytic oxidation 10 of BPA.<sup>28, 29</sup> Fig. 9B presents the catalytic performance of 5 wt% Cu-Al<sub>2</sub>O<sub>3</sub> membranes calcined at 11 different temperatures. The BPA removal percentages within 3 h were ~82%, ~100% and ~100% for 12 the membranes calcined at 600, 700 and 800 °C, respectively. The catalytic activities of the 13 membranes calcined at 700 and 800 °C increased obviously compared to 600 °C, which was due to 14 the higher BET surface areas (Fig. 6) and higher surface copper concentration (Fig. S4) at high 15 calcination temperatures. 16

The degradation efficiencies of BPA by various Cu-based catalysts are compared (Table S4). 17 Under the similar conditions, the BPA removal percentages were 98.3%, 100%, 90.4%, 87%, and 85% 18 by the copper-aluminum-silica nanospheres,<sup>14</sup> Mesoporous  $\gamma$ -Cu-Al<sub>2</sub>O<sub>3</sub> powders,<sup>13</sup> Mesoporous 19 Cu/TUD-1 powders,<sup>30</sup> 1 wt% Cu- Al<sub>2</sub>O<sub>3</sub>-600 membranes, and 5 wt% Cu- Al<sub>2</sub>O<sub>3</sub>-800 membranes, 20 respectively. The BPA degradation efficiencies by the Cu-Al<sub>2</sub>O<sub>3</sub> membrane catalysts are comparable 21 to those by the Cu-based powder catalysts. Advantageously, the membrane form Cu-Al<sub>2</sub>O<sub>3</sub> catalysts 22 23 need no extra separation after use, and the degradation can continuously proceed in the membrane reactor. Whereas, the powder form Cu-Al<sub>2</sub>O<sub>3</sub> catalysts usually disperse in water, and need filtration 24

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- 1 or centrifugation to separate them after use. Hence, the flexible Cu-Al<sub>2</sub>O<sub>3</sub> fibrous membranes have
- 2 an improvement over the state-of-the-art compared to the existing Fenton-like catalysts, and show
- 3 great potentials in waste water remediation area.
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Fig. 9 The influence of (A) Cu content on the BPA removal performance and (B) calcination
temperatures. Conditions: [BPA] = 20 mg/L, [H<sub>2</sub>O<sub>2</sub>] = 12 mM, initial pH = 7.

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The continuous batch-type degradation of BPA in the membrane reactor was evaluated. 9 Specifically, 10 mL BPA solution was added to the membrane reactor with the addition of 12 mM 10 H<sub>2</sub>O<sub>2</sub>. After more than 5 h, the solution was pulled out from the outlet, labeled as No. 1. Then, 11 12 another 10 mL BPA solution with 12 mM  $H_2O_2$  was added to the solution, and after more than 5 h, the solution was pulled out from the outlet, labeled as No. 2, and so on. The removal percentages of 13 the BPA solution were presented in Fig. 10. Compared to the 87% removal percentage of No. 1 14 solution, the removal percentages were decreased but still kept at  $\sim 67\%$  for the degradations toward 15 No.  $2 \sim No. 7$  solutions. The decrease of the catalytic activity was mainly occurred after the first time 16 use. According to the ICP-OES analysis, 0.151 mg L<sup>-1</sup> copper was leached during the first time use, 17 which reduced the copper active sites in the fibers, and it is considered to be the main reason for the 18 decrease of the catalytic activity. Notably, the leaching amount of Cu decreased to less than 0.01 mg 19  $L^{-1}$  over the third batch-type degradation. Hence the catalytic activity hardly changed for the second 20 to the seventh batch-type use, and the continuous treatment of bisphenol A could last at least 7 times. 21 22 Furthermore, the DMPO spin-trapping ESR results (Fig. 10B) confirmed the generation of •OH in the presence of  $Cu-Al_2O_3$  membranes with  $H_2O_2$ , demonstrating the Fenton catalytic activity of 23 Cu-Al<sub>2</sub>O<sub>3</sub> membranes. These results suggested that the Cu-Al<sub>2</sub>O<sub>3</sub> membranes are effective catalysts 24 for heterogeneous Fenton reactions, and can be used for continuous degradation of pollutant without 25 any extra separation or reclaim steps. 26



Fig. 10 (A) Continuous batch-type degradation of BPA in the membrane reactor, (B) DMPO
spin-trapping ESR spectra recorded at ambient temperature for 1 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600 fibrous
membranes.

To check the stability of the Cu-Al<sub>2</sub>O<sub>3</sub> membranes, the leaching of Cu and Al after 3 h reactions, 7 as well as the SEM and XPS of the membranes after use were tested. According to ICP-OES analysis, 8 the Cu leaching amounts were respectively 0.151, 0.172, 0.308, and 0.517 mg  $L^{-1}$  for 1 wt%, 3 wt%, 9 5 wt% and 7 wt% Cu-Al<sub>2</sub>O<sub>3</sub>-600 membranes, while the Al leaching amounts were remained ~0.18 10 mg L<sup>-1</sup> for all these membranes. Correspondingly, the Cu leaching percentages in the membranes are 11 respectively 1.51%, 0.43%, 0.64%, 0.61% for 1, 3, 5, 7 wt% Cu-Al<sub>2</sub>O<sub>3</sub> membranes, and the Al 12 leaching percentages are all remained 0.02% (the detailed computation process is in the supporting 13 information). The leaching percentages of Cu and Al are small, indicating that the Cu-Al<sub>2</sub>O<sub>3</sub> 14 membranes are relatively stable during use. Moreover, Both of Cu and Al leaching meet the standard 15 of drinking water, which regulate the limit of Cu is  $<1.0 \text{ mg L}^{-1}$ , and the limit of Al is  $<0.2 \text{ mg L}^{-1}$ 16 (GB 5750-85, China). Hence, there is negligible secondary pollution of the Cu-Al<sub>2</sub>O<sub>3</sub> membranes. 17 From the SEM images (Fig. S6), it can be seen that the membranes are still integrate without any 18 cracks after use. The XPS results of the membrane after use (Fig. S7 and the discussion in the 19 supporting information) are almost the same with that before use, except two small differences. One 20 difference is the disappear of  $SO_4^{2-}$  in the XPS survey spectrum, which is due to the dissolving of the 21 residual  $SO_4^{2-}$  on the surface of the fibers. The other difference is the peak of  $Cu^{2+}$  (935.1 eV) 22 becomes more evident, which is due to the  $Cu^{2+}/Cu^{+}$  cycles during reaction. These results prove that 23 the membranes are generally stable during use. 24

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### 1 3.3 Proposed mechanisms

Herein, the •OH generation mechanism via the Cu-Al<sub>2</sub>O<sub>3</sub> membrane catalysts as well as the 2 mechanistic pathway of bisphenol A in this system were proposed. The •OH generation mechanism 3 via the Cu-Al<sub>2</sub>O<sub>3</sub> membrane catalysts is shown in Fig. 11. Based on the XPS analysis, the Al-O-Cu is 4 existed in the fibers, and the chemical states of copper are  $Cu^+$  and  $Cu^{2+}$ . As shown in Fig. 11, the 5 action mechanism could be generally divided into three steps: In step (1), Cu<sup>+</sup> reacts with H<sub>2</sub>O<sub>2</sub> to 6 generate •OH, and along with the oxidization of  $Cu^+$  to  $Cu^{2+}$ ;<sup>13</sup> In step (2), BPA and  $Cu^{2+}$  in the 7 Cu-Al<sub>2</sub>O<sub>3</sub> membrane form the  $\sigma$ -Cu<sup>2+</sup>-ligands complexes via  $\sigma$ -bonding of Cu<sup>2+</sup> with the lone pairs of 8 the oxygen atom in the phenolic OH group.<sup>13, 31</sup> In the  $\sigma$ -Cu<sup>2+</sup>-ligands complexes,  $\pi \rightarrow Cu^{2+}$  electron 9 transfer occurs, which could on one hand reduce the Cu<sup>2+</sup> to Cu<sup>+</sup>, on the other hand increase the 10 electronic polarizability of the aromatic ring.<sup>13, 31</sup> In step (3), H<sub>2</sub>O<sub>2</sub> reacts with the aromatic ring that 11 chelated to Cu<sup>2+</sup>, and form the substituted aromatic species, which is a key intermediates.<sup>32, 33</sup> The 12  $H_2O_2$  interacted with the aromatic ring could on one hand discharge an electron to  $Cu^{2+}$  via the 13  $\sigma$ -Cu<sup>2+</sup>-ligands complexes, contributing to the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>, on the other hand form the 14 •OH radicals. These three steps possess synergistic effect. Therefore, the Cu<sup>2+</sup>/Cu<sup>+</sup> cycles are 15 succeeded on the surface of the Cu-Al<sub>2</sub>O<sub>3</sub> fibers, and •OH free radicals are well generated in this 16 17 catalytic system.



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Fig. 11 The •OH generation mechanism via the Cu-Al<sub>2</sub>O<sub>3</sub> membrane catalysts.

Hydroxyl radical (•OH) is an extraordinarily reactive species; it possesses strong oxidation ability with high oxidation potential ( $E^0=2.8 \text{ V}$ ), and can attack most organic molecules and mineralize them to nontoxic carbon dioxide and water.<sup>34, 35</sup> Herein, the intermediates in the reaction were identified (Table. S5 and the analysis in supporting information), and the mechanistic pathway of bisphenol A was proposed. As presented in Fig. 12, the reaction pathway was generally divided into three steps. In step (1), BPA was hydroxylated, or only one ring was occurred ring-opening reactions by the •OH attack and form the one-ring aromatic compounds, or decomposed into one-ring aromatic due to the cleavage of isopropylidene bridge by the •OH attack. In step (2), the aromatic ring was further cleavaged by the attack of •OH, leading to the formation of aliphatic acids. Finally, in step (3), all the organic intermediates were further oxidized and mineralized to  $CO_2$  and  $H_2O$  by the further attack of •OH. As a consequence, BPA was oxidized to  $CO_2$  and  $H_2O$  by the •OH attack in this reaction.



Fig. 12 A proposed degradation pathway of BPA in the reaction.

### 11 4. Conclusions

In summary, a novel Cu-Al<sub>2</sub>O<sub>3</sub> heterogeneous Fenton catalyst in the form of self-standing membrane has been successfully synthesized via electrospinning technique. The flexibility of the membrane is good and favorable for its practical applications. The copper exists in the form of Cu<sup>+</sup> and Cu<sup>2+</sup> in bulk alumina matrix with high evenly dispersion, providing much active sites in the fibrous membranes. Over 87% BPA was degraded within 180 min in the membrane reactor using the 1 wt% Cu-Al<sub>2</sub>O<sub>3</sub> membrane in neutral pH values with H<sub>2</sub>O<sub>2</sub> addition. This work opens up new avenues for the preparation and application of membranes with Fenton catalytic activities.

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# Graphical abstract

Flexible Cu-Al<sub>2</sub>O<sub>3</sub> membranes with high Fenton catalytic performance have been fabricated via electrospinning technique.

