Cite this: *J. Mater. Chem. A*, 2017, 5, 19151

Electrospun flexible self-standing Cu–Al₂O₃ fibrous membranes as Fenton catalysts for bisphenol A degradation†

Yan Wang, ^a Jiang Li,^{ab} Jianyang Sun,^a Yanbin Wang^a and Xu Zhao^{*ac}

Novel flexible self-standing Cu–Al₂O₃ fibrous membranes have been successfully synthesized *via* electrospinning technique, and they exhibited high Fenton catalytic activities under neutral pH values. The copper species are distributed uniformly in the fibers in the form of Cu⁺ and Cu²⁺, which was responsible for the Fenton catalytic performance. Over 87% of BPA was degraded within 180 min in the membrane reactor using the 1 wt% Cu–Al₂O₃ membrane at neutral pH values with H₂O₂ addition. The membranes can continuously degrade BPA by batch in the membrane reactor without any additional separation process. The excellent catalytic performance, good flexibility of the membranes, and the facile preparation process make the membranes good candidates for novel heterogeneous Fenton catalysts.

Received 19th May 2017
Accepted 16th August 2017

DOI: 10.1039/c7ta04386d

rsc.li/materials-a

1. Introduction

Recalcitrant organic pollutants are frequently detected in the water environment and are a serious health hazard to mankind.^{1,2} Developing an effective and practical method to remove organic pollutants is of significance and has recently become a research hotspot.^{3,4} Fenton processes are efficient advanced oxidation processes (AOPs) to remove organic pollutants from water.⁵ In the Fenton reaction, highly aggressive free hydroxyl radicals (•OH) are generated *via* the reduction of hydrogen peroxide (H₂O₂) with Fe²⁺ or other reducing transition metals.⁶ It is well known that there are two main limitations for the homogeneous Fenton process, which include the low pH range (3–5) required in the reaction as well as iron-containing sludge accumulation.^{7–9} As alternatives, heterogeneous Fenton catalysts could minimize the above disadvantages, and various kinds of heterogeneous catalysts, including supported gold nanoparticles,⁵ iron-containing solids,^{9–11} and bimetallic composites,¹² have been developed. However, mostly, the pH values of the solution still need to be adjusted to 3–5, and more exploration is needed of Fenton catalysts with high catalytic performance at neutral pH values.

Cu-based materials exhibit a Fenton catalytic activity with a wide pH range from 3 to 7. Up to now, various Cu-based Fenton catalysts such as Cu doped mesoporous γ-Al₂O₃ (γ-Cu–Al₂O₃),¹³ copper–aluminum–silica nanospheres,¹⁴ and Cu-containing zeolites,¹⁵ have been developed. Nevertheless, so far, the Cu-based heterogeneous Fenton catalysts are in scattered form in macrographs, usually disperse in water, and need filtration or centrifugation to separate them after use. Sometimes the incomplete separation will lead to possible catalyst lost and additional pollution to water.

Electrospun fibrous membranes are composed of nanofibers with small diameter, and many interconnected open pores exist in the membranes. Thus, the membranes possess good permeability and are favored in many environmental remediation areas.^{16,17} Meanwhile, the electrospinning technique offers a simple and versatile way to fabricate nanofibers, membranes and films from various materials.^{18–20} However, most inorganic membranes are fragile and transform to scattered form during use. Up to now, only a few kinds of flexible inorganic membranes have been developed *via* electrospinning method, such as SiO₂–TiO₂ composite membranes,¹⁷ silica/mesoporous alumina core-shell fibrous membranes²¹ and γ-alumina fibrous membranes.²² Most of these membranes are limited to adsorption or filtration performance. Membranes with catalytic performance still need further study. Therefore, research on fabricating membranes with a high Fenton catalytic activity is desired.

Herein, a novel flexible self-standing Cu–Al₂O₃ fibrous membrane was fabricated *via* electrospinning technique. The Cu–Al₂O₃ membrane was composed of randomly arranged nanofibers, and the copper species were distributed uniformly in the fibers. The membranes exhibited high Fenton catalytic

^aKey Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P. R. China. E-mail: zhaoxu@rcees.ac.cn

^bSchool of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, P. R. China

^cUniversity of Chinese Academy of Sciences, Beijing, P. R. China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ta04386d

activities, which suggested that the Cu–Al₂O₃ fibrous membranes are good candidates as Fenton catalysts.

2. Experimental section

2.1 Preparation procedure

All materials were analytical grade and commercially purchased without any further purification, including HCOOH, CH₃COOH, aluminum powder, polyethylene oxide (PEO, M_w = 500 000), polyvinylpyrrolidone (PVP, M_w = 1 300 000), and CuSO₄.

Preparation of alumina sol. The alumina sol was prepared according to our previous reports with some modifications.²² In a typical synthesis, 30.16 mL of HCOOH and 34.29 mL of CH₃COOH were dissolved in 86.4 mL of deionized water. Then, 5.4 g of 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 of colorless transparent alumina solution was obtained.

Preparation of copper–alumina electrospinning precursor. 10 mL of the alumina sol was taken in to a 25 mL beaker, then 0.035 g of PEO and 0.035 g of PVP were added and the solution was stirred for 2 h. Then 0.0408 g of CuSO₄ was added and stirred for 1 h to prepare the electrospinning precursor for the Cu–Al₂O₃ fibrous membrane with 1 wt% copper content, which was denoted as 1 wt% Cu–Al₂O₃. Similarly, 0.1224, 0.204 and 0.2856 g of CuSO₄ were respectively added to the 10 mL solution to prepare electrospinning precursors for the 3 wt%, 5 wt%, 7 wt% Cu–Al₂O₃ fibrous membranes.

Preparation of Cu–Al₂O₃ fibrous membrane. The electrospinning process was performed on a SS-2535H device (Ucalery Inc., Beijing, China) with the following parameters: 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^{−1}, the distance between the needle and the collector was 25.0 cm, the applied voltage was 12 kV, and the humidity was below 10%. After electrospinning, the xerogel fibrous membranes were obtained.

The xerogel fibrous membranes were calcined at high temperatures with a 1 °C min^{−1} heating rate and kept at the target temperature for 2 h. The membranes calcined at 600, 700 and 800 °C were denoted as Cu–Al₂O₃-600, Cu–Al₂O₃-700 and Cu–Al₂O₃-800, respectively.

2.2 Characterization

The morphology of the fibers was characterized on a field emission scanning electron microscope (SEM, SU-8020, Hitachi, Japan). Transmission electron microscopy (TEM) was performed by H7500 microscope (Hitachi, Japan). X-ray diffraction (XRD) was measured on an X'pert PRO MPD PC system using Cu K α (λ = 0.15 418 nm, 40 kV, 40 mA) as the X-ray source. X-ray photoelectron spectroscopy (XPS) was performed on a Phi Quantern instrument. The binding energy (BE) measurements were calibrated for charging effects with the C 1s peak (284.8 eV)

as the reference. Thermo-gravimetric (TG) and differential scanning calorimetry (DSC) measurements were carried out on a Mettler TGA-1 thermogravimetric analyzer with a heating rate of 10 °C min^{−1} and up to 1000 °C in air atmosphere. The diffuse reflectance absorption spectra (DRS) were investigated in the range from 200 to 800 nm on a Maya 2000 Pro (Oceanoptics Inc.) spectroscope. N₂ adsorption–desorption isotherms were tested on a Quadrasorb SI apparatus. All the membranes were degassed at 200 °C under vacuum for 5 h before analysis.

2.3 Fenton oxidation experiments

The Fenton catalytic performance of the Cu–Al₂O₃ membranes was tested by fixing 10 mg of membrane in the membrane reactor. 10 mL of BPA aqueous solution (20 mg L^{−1}) was added into the reactor, and then stirred to establish adsorption/desorption equilibrium. Then, 12 mM of H₂O₂ was added and the solution kept stirring unless otherwise specified. At appropriate time intervals, 0.50 mL of solution was collected and mixed with 500 μ L of methanol to quench the residual $\cdot$ OH, and then filtered through a Millipore filter (pore size 0.45 μ m) for HPLC analysis.

The samples were analyzed using a HPLC (LC-20AT, Shimadzu) equipped with a C₁₈ reversed-phase column (250 mm $\times$ 4.6 mm, 5 μ m, GL, Science Inc.) and a UV detector (λ = 280 nm). The mobile phase consisted of a 70/30 v/v mixture of methanol/water at a flow rate of 1 mL min^{−1}. 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 (Optima 2000, PerkinElmer Co., USA). The electron spin-resonance (ESR) spectra were recorded on a Bruker A 300-10/12 ESR spectrometer at room temperature and DMPO was used as the spin trap agent.

The intermediates of BPA degradation were identified by UPLC-Q-TOF-MS (ACQUITY UPLC, Quattro Premier XE, Waters, USA) with a C₁₈ column (2.1 mm $\times$ 50 mm $\times$ 1.7 μ m). The mobile phase containing A (Milli-Q water) and B (methanol) was delivered at 0.3 mL min^{−1}. 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.

3. Results and discussion

3.1 Fabrication and morphology of Cu–Al₂O₃ membranes

The formation of Cu–Al₂O₃ fibrous membranes involves several processes. As shown in Fig. 1, the alumina powder was reacted with carboxylic acid to acquire a stable homogeneous alumina solution.²² Then, small amounts of PVP and PEO were added to respectively adjust the spinnability and viscosity of the alumina solution, and CuSO₄ was dissolved in the solution. Hence, a light blue transparent electrospinning precursor containing evenly distributed Cu²⁺ and Al³⁺ was formed. During the electrospinning process, the solvent evaporates rapidly, leading to the immediate formation of Cu–Al₂O₃ nanofibers with high

Fig. 1 Schematic illustration of the formation of the Cu–Al₂O₃ membrane.

aspect ratio. The electrospinning method can avoid the long evaporation of solvents by the evaporation-induced self-assembly method that is involved in most of the literature, and can directly obtain the membrane form catalysts. The details of the methods for preparing Cu–Al₂O₃ catalysts are discussed in the ESI.† As shown in Fig. S1A,† SEM images indicate that the fibers are continuous with high aspect ratios. The average diameter is *ca.* 500 nm. TG-DSC curves (Fig. S1B†) of the xerogel membranes indicate that the mass loss (65.05%) mainly occurred before 500 °C, which was caused by the decomposition of organics as well as the removal of H₂O. Correspondingly, three exothermic peaks in the range of 30–500 °C are observed in the DSC curves. Hence, the calcination temperatures were chosen to be above 500 °C. After calcination, the flexible Cu–Al₂O₃ membranes were formed, and the –Al–O–Cu– chemical bond was assumed to have formed in the fibers.

The morphology and microstructure of the Cu–Al₂O₃-600 membranes are presented in Fig. 2. The membranes could be bent many times and remained integrated without any cracks, demonstrating that the membranes possess excellent flexibility. The SEM image shows that the membranes are uniformly composed of randomly oriented nanofibers. There are many interconnected open pores in the membranes, which is beneficial for the permeability of the membranes. Fig. S2† presents the SEM images of the Cu–Al₂O₃ membranes with various Cu contents and calcined at various temperatures. It can be seen

Fig. 3 EDS of a single fiber of 5 wt% Cu–Al₂O₃-600.

that all the membranes are composed of randomly arranged nanofibers. The average fiber diameters for the membranes calcined at 600 °C are slightly decreased with increasing Cu content at 390, 360, 340 and 320 nm for 1, 3, 5, 7 wt% Cu–Al₂O₃ fibrous membranes, respectively (Table S1†). Meanwhile, with the increasing calcination temperatures, the average fiber diameter decreased obviously with 340, 270, and 190 nm for 5 wt% Cu–Al₂O₃ membranes calcined at 600, 700 and 800 °C, respectively (Table S1†). STEM images (Fig. 2B) indicate that the fibers are homogeneous without any particles or other phases, indicating that the copper species distribute homogeneously in the fibers instead of forming copper or copper oxide particles. The surfaces of the fibers are smooth without any cracks, which is beneficial for membrane flexibility. TEM images (Fig. 2C) further demonstrate the homogeneity of the fibers.

EDS analysis of a single fiber was carried out to identify the element distribution. In Fig. 3, three elements including Al, O and Cu are observed and distributed uniformly. The copper wire mesh was used for preparing the samples for analysis, thus some Cu elements were detected outside the fiber. The homogeneous distribution of copper element is beneficial for its sufficient contact with the target pollutants in water and is thus in favor of the catalytic process. Moreover, the EDS spectrum of the membrane was tested to give an overall analysis of the

Fig. 2 (A) SEM image, (B) STEM image and (C) TEM image of 5 wt% Cu–Al₂O₃-600 membrane. The inset in (A) is an optical image and the inset in (C) is an HRTEM image of the membrane.

elements in the fibers. As presented in Fig. S3,[†] five elements, Al, O, Cu, S and Au, were observed. Among them, Al, O, and Cu are the main elements of the Cu-Al₂O₃ membranes. Au is derived from the Au spraying pretreatment, which could enhance the conductivity of the Cu-Al₂O₃ membrane to get a high quality of SEM image. A small amount of S element is also observed between 2–3 kV, and it is due to the incomplete removal of SO₄²⁻ that was introduced by CuSO₄. According to previous reports, H₂SO₄ is often used as common acid-base regulator to control the pH of the solution because SO₄²⁻ rarely affects the degradation.²³ Hence, the small amount of residual SO₄²⁻ in the fibers is considered to have a negligible effect on the catalytic performance of the Cu-Al₂O₃ membranes. Moreover, the concentration of Cu element in the fiber is 6.59 wt% (Table S2[†]), similar to but not the same as the calculated concentration (5 wt%) owing to the semi-quantitative nature of the EDS analysis.

XRD (Fig. 4A) analysis was performed to identify the crystal phase of the membranes. As for the xerogel fibrous membranes and the membranes calcined at 600 °C, no peaks but humps could be observed in the XRD patterns, indicating that the phases are amorphous. The peaks of γ -alumina (PDF card number: 50-0741) appeared when the membranes were calcined at 700 °C, and the crystallinity improved when the calcination temperature was increased to 800 °C. In addition, it is worth noting that no copper and copper-related diffraction peaks appeared for all the samples, indicating that copper species with the individual crystal phase were not formed. In the UV-Vis spectra (Fig. 4B), no obvious absorptions were observed for individual Al₂O₃ membranes, while for Cu-Al₂O₃ membranes calcined at 600 and 800 °C, an absorption peak at 750 nm was observed and attributed to the electron transitions in Cu²⁺ in the alumina lattice,²⁴ which confirmed that the copper species was mostly incorporated in the alumina matrix.

The complete information on the surface of the Cu-Al₂O₃ membranes was identified by the XPS survey spectrum. As shown in Fig. 5A, peaks of Al, O, Cu, S and C in the XPS survey spectrum of the 5 wt% Cu-Al₂O₃-600 membrane are observed. Among them, Al, O, and Cu are the main elements of the membranes. The S element is derived from the residual SO₄²⁻ in the membrane, and this is consistent with the EDS analysis (Fig. S3[†]). The peak of C element appeared unavoidably owing

Fig. 5 XPS analysis of the 5 wt% Cu-Al₂O₃-600 membrane: (A) XPS survey, (B) Cu 2p and (C) Al 2p spectra.

to the adsorbed CO₂ from air. In addition, the peaks of S element are absent in the XPS survey spectrum of the 5 wt% Cu-Al₂O₃-800 membrane (Fig. S4[†]), indicating that SO₄²⁻ is totally removed when the membrane is calcined at 800 °C.

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 C). In the Cu 2p spectra, the peak centred at 933.1 eV corresponds to the reduced state of copper species. The Auger kinetic energy at 914.6 eV based on AES measurements confirmed that the reduced state of copper was Cu⁺. The peak assigned to the oxidized state of copper was observed at 935.1 eV, and the shakeup satellite line at 942.8 eV also appeared, confirming the presence of Cu²⁺. The atomic ratio of Cu⁺ to Cu²⁺ 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⁺ and Cu²⁺. The XPS spectra of Al 2p was fitted to two peaks centered at 74.2 and 75.3 eV, ascribed to Al-O-Al and Al-O-Cu, respectively. 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.²⁵ According to previous reports,²⁶ the dispersed copper species in the bulk alumina matrix can introduce oxygen vacancies (V_O) and other intrinsic defects, which may result in excess electrons caused by charge compensation. The excess electrons could stimulate the reducing transformation from Cu²⁺ to Cu⁺, and stabilize the Cu⁺ by avoiding its oxidization. Moreover, it is worth noting that 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 fiber surface due to the rearrangement of Al, O and Cu atoms during crystallization.

N₂ adsorption-desorption isotherms of the membranes were obtained to shed some light on the BET surface area of the

Fig. 4 (A) XRD patterns of the 5 wt% Cu-Al₂O₃ membranes calcined at various temperatures and (B) UV-Vis DRS of individual Al₂O₃ and 5 wt% Cu-Al₂O₃ membranes.

Fig. 6 N₂ adsorption-desorption isotherms of (A) Cu-Al₂O₃-600 membranes with various copper contents and (B) 5 wt% Cu-Al₂O₃ membranes calcined at various temperatures.

membranes. In Fig. 6A, all the Cu-Al₂O₃-600 membranes with various copper contents exhibited type III-like adsorption isotherms, which corresponds to the adsorption of N₂ on nonporous materials.²¹ As shown in Table S3,† the BET surface areas were 12.33, 9.26, 10.10 and 8.11 m² g⁻¹ for the 1 wt%, 3 wt%, 5 wt% and 7 wt% Cu-Al₂O₃-600 membranes, respectively. These results indicate that the effect of copper content on the surface area of the Cu-Al₂O₃ membranes is very small. The surface areas of the 5 wt% Cu-Al₂O₃ membranes calcined at various temperatures were also tested. As shown in Fig. 6B, when the calcination temperature increased to 700 and 800 °C, the membranes exhibited type IV-like adsorption branches, indicating the existence of mesopores in the fibers.^{22,27} The BET surface areas were 10.10, 40.56, 38.63 m² g⁻¹ for the 5 wt% Cu-Al₂O₃ membranes calcined at 600, 700 and 800 °C, respectively. The BET surface area increased when the calcination temperature increased from 600 to 700 °C, and then changed very little from 700 to 800 °C. The higher surface area could provide more active sites and increase the contact area of the active sites and the pollutants, hence improving the degradation rate.

3.2 Catalytic performance of Cu-Al₂O₃ membranes

The Fenton-like catalytic performance of the Cu-Al₂O₃ membranes was evaluated by using bisphenol A (BPA) as the target pollutant, which is a representative endocrine disrupter. Specifically, a membrane reactor (Fig. 7) was used for the Fenton reactions. The membranes were cut into a round shape to match the reactor, and then fixed in the bottom of the reactor. Prior to the main experiments, the reaction was optimized by

Fig. 7 (A) Illustration of the membrane reactor and (B) picture of a 5 wt% Cu-Al₂O₃-600 membrane.

varying the H₂O₂ dosage as it is a key factor that influences the Fenton reaction.¹³ The detailed analysis is shown Fig. S5† and is discussed in the ESI.† The results indicate that 12 mM was the optimal H₂O₂ dosage in this reaction, and 12 mM H₂O₂ was used in all experiments unless otherwise specified. Fig. 8 presents the results of the Fenton catalytic performance toward BPA degradation under various conditions. In Fig. 8A, nearly no removal of BPA was observed with individual H₂O₂ addition. Meanwhile, ~3% BPA was removed due to the adsorption by the individual membranes, and the adsorption equilibrium established within 30 min. Notably, 82% BPA was removed by the 5 wt% Cu-Al₂O₃-600 membranes using the membrane reactor with the addition of H₂O₂, while under the same conditions ~84% BPA was removed by stirring the membranes in a beaker and forming the conventional suspension. The difference in the removal ability of the membrane reaction and the suspension form is slight, suggesting that the molecular mass transfer rate in the membrane reactor is still fast and has little effect on the catalytic process. Moreover, the effects of initial pH on the Fenton catalytic performance were investigated. The initial pH values were adjusted by 0.1 M H₂SO₄. As shown in Fig. 8B, ~86% BPA was removed within 180 min at pH 3, 5 and 7. Neutral pH values are favorable in practical applications because there is no need to adjust the pH. Therefore, the pH of 7 was chosen as the optimal condition for further investigations.

Fig. 9A presents the catalytic performance of the Cu-Al₂O₃-600 membranes with various Cu contents. It can be seen that ~15% BPA was removed by the individual Al₂O₃-600 membrane, while 87%, 82%, 84% and 93% BPA were removed by the 1, 3, 5 and 7 wt% Cu-Al₂O₃-600 membranes, respectively. The degradation ability of the membranes with 1–7 wt% Cu content are all satisfactory. Correspondingly, the TOC removal percentages were 59.8%, 52.1%, 57.8% and 63.20% for 1, 3, 5 and 7 wt% Cu-Al₂O₃-600 membranes, respectively. These TOC removal percentages were much higher than those in previous reports (10–30%) under similar conditions for Fenton catalytic oxidation of BPA.^{28,29} Fig. 9B presents the catalytic performance of the 5 wt% Cu-Al₂O₃ membranes calcined at different temperatures. The BPA removal percentages within 3 h were ~82%, ~100% and ~100% for the membranes calcined at 600, 700 and 800 °C, respectively. The catalytic activities of the membranes calcined at 700 and 800 °C increased obviously compared to the membrane calcined at 600 °C, which was due to the higher BET

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-Al₂O₃-600 membranes. Conditions: [BPA] = 20 mg L⁻¹, [H₂O₂] = 12 mM.

Fig. 9 The influence of (A) Cu content on the BPA removal performance and (B) calcination temperatures. Conditions: [BPA] = 20 mg L⁻¹, [H₂O₂] = 12 mM, initial pH = 7.

surface areas (Fig. 6) and higher surface copper concentration (Fig. S4†) at higher calcination temperatures.

The degradation efficiencies of BPA by various Cu-based catalysts are compared (Table S4†). Under similar conditions, the BPA removal percentages were 98.3%, 100%, 90.4%, 87%, and 85% by the copper-aluminum-silica nanospheres,¹⁴ mesoporous γ -Cu-Al₂O₃ powders,¹³ mesoporous Cu/TUD-1 powders,³⁰ 1 wt% Cu-Al₂O₃-600 membranes, and 5 wt% Cu-Al₂O₃-800 membranes, respectively. The BPA degradation efficiencies by the Cu-Al₂O₃ membrane catalysts are comparable to those by the Cu-based powder catalysts. Advantageously, the membrane form Cu-Al₂O₃ catalysts need no extra separation after use, and the degradation can continuously proceed in the membrane reactor. Conversely, the powder form Cu-Al₂O₃ catalysts usually disperse in water and need filtration or centrifugation to separate them after use. Hence, the flexible Cu-Al₂O₃ fibrous membranes offer an improvement over the state-of-the-art compared to the existing Fenton-like catalysts, and show great potential in the waste water remediation area.

The continuous batch-type degradation of BPA in the membrane reactor was evaluated. Specifically, 10 mL of BPA solution was added to the membrane reactor with the addition of 12 mM H₂O₂. After more than 5 h, the solution was pulled out from the outlet, labeled as No. 1. Then, another 10 mL of BPA solution with 12 mM H₂O₂ 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 the BPA solution are presented in Fig. 10. Compared to the 87% removal

percentage of the No. 1 solution, the removal percentages were decreased but still kept at ~67% for the degradations toward the No. 2 to No. 7 solutions. The decrease of the catalytic activity mainly occurred after the first use. According to the ICP-OES analysis, 0.151 mg L⁻¹ copper was leached during the first use, which reduced the copper active sites in the fibers, and it is considered to be the main reason for the decrease of the catalytic activity. Notably, the leaching amount of Cu decreased to less than 0.01 mg L⁻¹ over the third batch-type degradation. Hence the catalytic activity hardly changed for the second to the seventh batch-type use, and the continuous treatment of bisphenol A could be carried out at least seven times. Furthermore, the DMPO spin-trapping ESR results (Fig. 10B) confirmed the generation of $\cdot\text{OH}$ in the presence of Cu-Al₂O₃ membranes with H₂O₂, demonstrating the Fenton catalytic activity of the Cu-Al₂O₃ membranes. These results suggested that the Cu-Al₂O₃ membranes are effective catalysts for heterogeneous Fenton reactions, and can be used for continuous degradation of pollutants without any extra separation or reclamation steps.

To check the stability of the Cu-Al₂O₃ membranes, the leaching of Cu and Al after 3 h reactions, as well as the SEM and XPS of the membranes after use were tested. According to ICP-OES analysis, the Cu leaching amounts were 0.151, 0.172, 0.308, and 0.517 mg L⁻¹ for 1 wt%, 3 wt%, 5 wt% and 7 wt% Cu-Al₂O₃-600 membranes, respectively, while the Al leaching amounts remained at ~0.18 mg L⁻¹ for all these membranes. Correspondingly, the Cu leaching percentages in the membranes were 1.51%, 0.43%, 0.64%, and 0.61% for 1, 3, 5, and 7 wt% Cu-Al₂O₃ membranes, respectively, and the Al leaching percentages all remained at 0.02% (the detailed computation process is in the ESI†). The leaching percentages of Cu and Al are small, indicating that the Cu-Al₂O₃ membranes are relatively stable during use. Moreover, both Cu and Al leaching met the drinking water standard, which gives the limit of Cu as <1.0 mg L⁻¹ and the limit of Al as <0.2 mg L⁻¹ (GB 5750-85, China). Hence, there is negligible secondary pollution from the Cu-Al₂O₃ membranes. From the SEM images (Fig. S6†), it can be seen that the membranes are still integrated without any cracks after use. The XPS results of the membrane after use (Fig. S7 and the discussion in the ESI†) are almost the same as those before use, except for two small differences. One difference is the disappearance of SO₄²⁻ in the XPS survey spectrum, which is owing to the dissolving of the residual SO₄²⁻ on the

Fig. 10 (A) Continuous batch-type degradation of BPA in the membrane reactor and (B) DMPO spin-trapping ESR spectra recorded at ambient temperature for 1 wt% Cu-Al₂O₃-600 fibrous membranes.

Fig. 11 The $\cdot\text{OH}$ generation mechanism via the Cu-Al₂O₃ membrane catalysts.

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

surface of the fibers. The other difference is that the peak of Cu^{2+} (935.1 eV) becomes more evident, which is due to the $\text{Cu}^{2+}/\text{Cu}^+$ cycles during the reaction. These results prove that the membranes are generally stable during use.

3.3 Proposed mechanisms

Herein, the $\cdot\text{OH}$ generation mechanism *via* the $\text{Cu-Al}_2\text{O}_3$ membrane catalysts as well as the mechanistic pathway of bisphenol A in this system are proposed. The $\cdot\text{OH}$ generation mechanism *via* the $\text{Cu-Al}_2\text{O}_3$ membrane catalysts is shown in Fig. 11. Based on the XPS analysis, the Al-O-Cu is present in the fibers, and the chemical states of copper are Cu^+ and Cu^{2+} . As shown in Fig. 11, the reaction mechanism could be generally divided into three steps: In step ①, Cu^+ reacts with H_2O_2 to generate $\cdot\text{OH}$, along with the oxidation of Cu^+ to Cu^{2+} .¹³ In step ②, BPA and Cu^{2+} in the $\text{Cu-Al}_2\text{O}_3$ membrane form the $\sigma\text{-Cu}^{2+}$ -ligands complexes *via* σ -bonding of Cu^{2+} with the lone pairs of the oxygen atom in the phenolic OH group.^{13,31} In the $\sigma\text{-Cu}^{2+}$ -ligands complexes, $\pi \rightarrow \text{Cu}^{2+}$ electron transfer occurs, which could on one hand reduce the Cu^{2+} to Cu^+ , or on the other hand increase the electronic polarizability of the aromatic ring.^{13,31} In step ③, H_2O_2 reacts with the aromatic ring that is chelated to Cu^{2+} , and forms the substituted aromatic species, which is a key intermediate.^{32,33} The H_2O_2 interacting with the aromatic ring could on one hand discharge an electron to Cu^{2+} *via* the $\sigma\text{-Cu}^{2+}$ -ligands complexes, contributing to the reduction of Cu^{2+} to Cu^+ , or on the other hand form the $\cdot\text{OH}$ radicals. These three steps have a synergistic effect. Therefore, the $\text{Cu}^{2+}/\text{Cu}^+$ cycles are carried out on the surface of the $\text{Cu-Al}_2\text{O}_3$ fibers, and $\cdot\text{OH}$ free radicals are well generated in this catalytic system.

The hydroxyl radical ($\cdot\text{OH}$) is an extraordinarily reactive species; it possesses strong oxidation ability with high oxidation potential ($E^0 = 2.8$ V), and can attack most organic molecules and mineralize them to nontoxic carbon dioxide and water.^{34,35} Herein, the intermediates in the reaction were identified (Table S5 and the analysis in the ESI[†]), and the mechanistic pathway of bisphenol A is 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 subjected to ring-

opening reaction by the $\cdot\text{OH}$ attack and formed the one-ring aromatic compounds, or decomposed into a one-ring aromatic due to the cleavage of isopropylidene bridge by the $\cdot\text{OH}$ attack. In step ②, the aromatic ring was further cleaved by the attack of $\cdot\text{OH}$, 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 $\cdot\text{OH}$. As a consequence, BPA was oxidized to CO_2 and H_2O by the $\cdot\text{OH}$ attack in this reaction.

4. Conclusions

In summary, a novel $\text{Cu-Al}_2\text{O}_3$ heterogeneous Fenton catalyst in the form of a 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^+ and Cu^{2+} in the bulk alumina matrix with very even dispersion, providing many active sites in the fibrous membranes. Over 87% of BPA was degraded within 180 min in the membrane reactor using the 1 wt% $\text{Cu-Al}_2\text{O}_3$ membrane at neutral pH with the addition of H_2O_2 . This work opens up new avenues for the preparation and application of membranes with Fenton catalytic activities.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by projects of the National Key Research and Development Program of China (No. 2016YFA0203101) and the Beijing Natural Science Foundation (No. 8174076).

References

- 1 G. Zhao, L. Jiang, Y. He, J. Li, H. Dong, X. Wang and W. Hu, *Adv. Mater.*, 2011, **23**, 3959–3963.
- 2 N. Wang, L. Zhu, M. Lei, Y. She, M. Cao and H. Tang, *ACS Catal.*, 2011, **1**, 1193–1202.

- 3 N. N. Tušar, D. Maučec, M. Rangus, I. Arčon, M. Mazaj, M. Cotman, A. Pintar and V. Kaučič, *Adv. Funct. Mater.*, 2012, **22**, 820–826.
- 4 C.-C. Wang, J.-R. Li, X.-L. Lv, Y.-Q. Zhang and G. Guo, *Energy Environ. Sci.*, 2014, **7**, 2831–2867.
- 5 S. Navalon, R. Martin, M. Alvaro and H. Garcia, *Angew. Chem., Int. Ed.*, 2010, **49**, 8403–8407.
- 6 S. Navalon, M. de Miguel, R. Martin, M. Alvaro and H. Garcia, *J. Am. Chem. Soc.*, 2011, **133**, 2218–2226.
- 7 M. Hermanek, R. Zboril, I. Medrik, J. Pechousek and C. Gregor, *J. Am. Chem. Soc.*, 2007, **129**, 10929–10936.
- 8 H. Lim, J. Lee, S. Jin, J. Kim, J. Yoon and T. Hyeon, *Chem. Commun.*, 2006, 463–465.
- 9 X. J. Yang, X. M. Xu, J. Xu and Y. F. Han, *J. Am. Chem. Soc.*, 2013, **135**, 16058–16061.
- 10 R. Gonzalez-Olmos, M. J. Martin, A. Georgi, F.-D. Kopinke, I. Oller and S. Malato, *Appl. Catal., B*, 2012, **125**, 51–58.
- 11 G. Zhang, Y. Gao, Y. Zhang and Y. Guo, *Environ. Sci. Technol.*, 2010, **44**, 6384–6389.
- 12 Y. Wang, H. Zhao and G. Zhao, *Appl. Catal., B*, 2015, **164**, 396–406.
- 13 L. Lyu, L. Zhang, Q. Wang, Y. Nie and C. Hu, *Environ. Sci. Technol.*, 2015, **49**, 8639–8647.
- 14 L. Lyu, L. Zhang, C. Hu and M. Yang, *J. Mater. Chem. A*, 2016, **4**, 8610–8619.
- 15 M. Dükkancı, G. Gündüz, S. Yılmaz and R. V. Prihod'ko, *J. Hazard. Mater.*, 2010, **181**, 343–350.
- 16 R. Gopal, S. Kaur, Z. Ma, C. Chan, S. Ramakrishna and T. Matsuura, *J. Membr. Sci.*, 2006, **281**, 581–586.
- 17 Q. Wen, J. Di, Y. Zhao, Y. Wang, L. Jiang and J. Yu, *Chem. Sci.*, 2013, **4**, 4378–4382.
- 18 C. L. Zhang and S. H. Yu, *Chem. Soc. Rev.*, 2014, **43**, 4423–4448.
- 19 R. Sridhar, R. Lakshminarayanan, K. Madhaiyan, V. Amutha Barathi, K. H. Lim and S. Ramakrishna, *Chem. Soc. Rev.*, 2015, **44**, 790–814.
- 20 P. S. Kumar, J. Sundaramurthy, S. Sundarrajan, V. J. Babu, G. Singh, S. I. Allakhverdiev and S. Ramakrishna, *Energy Environ. Sci.*, 2014, **7**, 3192–3222.
- 21 Y. Wang, W. Ding, X. Jiao and D. Chen, *RSC Adv.*, 2014, **4**, 30790–30797.
- 22 Y. Wang, W. Li, Y. Xia, X. Jiao and D. Chen, *J. Mater. Chem. A*, 2014, **2**, 15124–15131.
- 23 Y. Lei, C. S. Chen, Y. J. Tu, Y. H. Huang and H. Zhang, *Environ. Sci. Technol.*, 2015, **49**, 6838–6845.
- 24 K.-I. Shimizu, H. Kawabata, H. Maeshima, A. Satsuma and T. Hattori, *J. Phys. Chem. B*, 2000, **104**, 2885–2893.
- 25 L. Yang, C. Hu, Y. Nie and J. Qu, *Environ. Sci. Technol.*, 2009, **43**, 2525–2529.
- 26 L. Fu, X. Li, M. Liu and H. Yang, *J. Mater. Chem. A*, 2013, **1**, 14592–14605.
- 27 M. Kruk and M. Jaroniec, *Chem. Mater.*, 2001, **13**, 3169–3183.
- 28 R. A. Torres, F. Abdelmalek, E. Combet, C. Petrier and C. Pulgarin, *J. Hazard. Mater.*, 2007, **146**, 546–551.
- 29 R. Huang, Z. Fang, X. Yan and W. Cheng, *Chem. Eng. J.*, 2012, **197**, 242–249.
- 30 M. P. Pachamuthu, S. Karthikeyan, R. Maheswari, A. F. Lee and A. Ramanathan, *Appl. Surf. Sci.*, 2017, **393**, 67–73.
- 31 A. Lagutschenkov, R. K. Sinha, P. Maitre and O. Dopfer, *J. Phys. Chem. A*, 2010, **114**, 11053–11059.
- 32 S. Goldstein, G. Czapski and J. Rabani, *J. Phys. Chem.*, 1994, **98**, 6586–6591.
- 33 C. Walling, D. M. Camaioni and S. S. Kim, *J. Am. Chem. Soc.*, 1978, **100**, 4814–4818.
- 34 F. Ghanbari and M. Moradi, *Chem. Eng. J.*, 2017, **310**(1), 41–62.
- 35 R. A. Torres, J. I. Nieto, E. Combet, C. Pétrier and C. Pulgarin, *Appl. Catal., B*, 2008, **80**, 168–175.