Carbohydrate Polymers 92 (2013) 2041–2047

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Novel spider-web-like nanoporous networks based on jute cellulose nanowhiskers

Xinwang Cao[a,b,c], Xianfeng Wang[a,b], Bin Ding[b,d,*], Jianyong Yu[b,*], Gang Sun[b]

[a] College of Textiles, Donghua University, Shanghai 201620, China
[b] Nanomaterials Research Center, Research Institute of Donghua University, Shanghai 200051, China
[c] College of Textiles, Wuhan Textile University, Wuhan 430073, China
[d] College of Materials Science and Engineering, Wuhan Textile University, Wuhan 430073, China

ARTICLE INFO

Article history:
Received 30 October 2012
Received in revised form
23 November 2012
Accepted 26 November 2012
Available online 3 December 2012

Keywords:
Jute cellulose nanowhiskers
Electrospun nanofibrous membrane
Nanoporous networks
Silica nanofibrous membrane

ABSTRACT

Cellulose nanowhiskers as a kind of renewable and biocompatible nanomaterials evoke much interest because of its versatility in various applications. Herein, for the first time, a novel controllable fabrication of spider-web-like nanoporous networks based on jute cellulose nanowhiskers (JCNs) deposited on the electrospun (ES) nanofibrous membrane by simple directly immersion-drying method is reported. Jute cellulose nanowhiskers were extracted from jute fibers with a high yield (over 80%) via a 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)/NaBr/NaClO system selective oxidization combined with mechanical homogenization. The morphology of JCNs nanoporous networks/ES nanofibrous membrane architecture, including coverage rate, pore-width and layer-by-layer packing structure of the nanoporous networks, can be finely controlled by regulating the JCNs dispersions properties and drying conditions. The versatile nanoporous network composites based on jute cellulose nanowhiskers with ultrathin diameters (3–10 nm) and nanofibrous membrane supports with diameters of 100–300 nm, would be particularly useful for filter applications.

1. Introduction

Recently, cellulose nanowhiskers or nanocrystals have attracted wide attention because of their super functionalities for various applications, e.g., green nanocomposites, optically transparent functional materials, filtering media (Burger, Hsiao, & Chu, 2006; Ma, Burger, Hsiao, & Chu, 2011), tissue engineering scaffolds (Svensson et al., 2005), catalysts, textiles, surface coatings (Cao, Ding, Yu, & Al-Deyab, 2013), drug delivery, and food packaging, due to their extremely large and active surface areas (Wagberg et al., 2008).

As we all known, cellulose is widely present as crystalline nanofibrils with extremely small widths of about 4 nm in plant cell walls, which has plentiful resource in nature (Kristin & Per, 2009). Cellulose nanowhiskers suspensions could be prepared from natural cellulose such as wood pulps, cotton linters (Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006), jute fibers (Cao, Ding, Yu, & Al-Deyab, 2012), and so on, with a special high yield (more than 80%), through 2,2,6,6-tetramethylpoperidine-1-oxyl (TEMPO)/NaBr/NaClO oxidization.

Network structure materials with nanosized pores had great potential applications as high efficient filter in air, food, and medical fields (Ding, Wang, Wang, Yu, & Sun, 2010; Wang, Ding, Yu, & Wang, 2011). During our previous work, we prepared nanofibers/nets membranes using different kinds of polymer solutions by one step elctro spinning/netting process (Hu et al., 2011; Wang, Wang, Ding, Yu, & Sun, 2012; Wang et al., in press). Cellulose nanowhiskers with ultra-thin diameters are promising to prepare new bio-based and environmental friendly porous network materials with high performance. Through supercritical drying and freeze-drying, the porous nanofibril networks aerogels with high specific areas, low densities and better mechanical properties than those of other organic polymers, could be obtained from aqueous cellulose nanowhiskers suspensions (Saito, Uematsu, Kimura, Enomae, & Isogai, 2011; Svagan, Samir, & Berglund, 2008). However, both methods require special equipments and/or solvent exchange process, which is time consuming, costly, extremely low productive, and even harmful to the environment. Therefore, more simple and high productive processes would be desirable for the preparation of nanowhiskers porous networks.

In the present investigation, cellulose nanowhiskers extracted from chemically pretreated jute fibers by the combination of TEMPO/NaBr/NaClO system selective oxidization and mechanical

---

* Corresponding authors at: Nanomaterials Research Center, Research Institute of Donghua University, Shanghai 200051, China. Tel.: +86 21 6237 8202; fax: +86 21 6237 8392.
E-mail addresses: binding@dhu.edu.cn (B. Ding), yujy@dhu.edu.cn (J. Yu).

0144-8617/$ – see front matter. Crown Copyright © 2012 Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.11.085

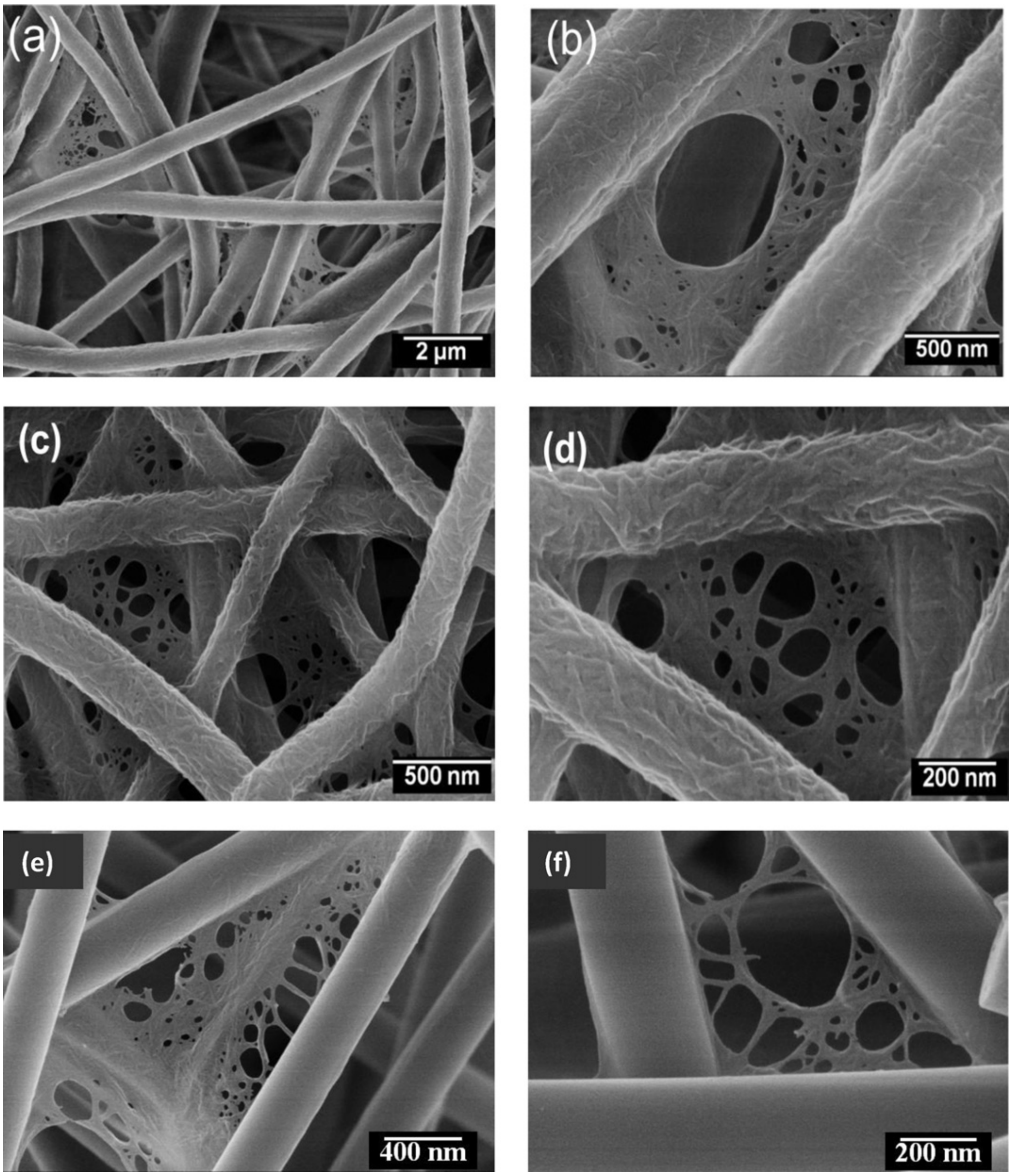

Fig. 1. FE-SEM images of porous JCNs networks in different nanofibrous membranes: (a and b) PAN, (c and d) PVA, and (e and f) silica.

homogenization were deposited on electrospun nanofibrous membranes and formed into ultrathin nanoporous networks by simple immersing-drying process. The effects of jute cellulose nanowhiskers suspensions and drying conditions on the morphologies of nanoporous networks in the composite membranes were investigated by field-emission scanning electron microraph.

2. Experimental

2.1. Raw materials

Jute bast fibers (Redbud Textile Tech. Inc., Jiangsu, China) were sieved under 60 mesh and vacuum dried before used. The starting materials included polyacrylonitrile (PAN, Mw = 90, 000, Spectrum Chemical Co., Ltd., USA), poly (vinyl alcohol) (PVA, Mw = 88, 000, Aladdin Chemical Regents Co., Ltd., China), tetraethyl orthosilicate (TEOS, Lingfeng Chemical Co., Ltd., China), phosphoric acid (H_3PO_4, Shanghai Chemical Reagents Co., Ltd., China). NaOH, dimethylsulfoxide (DMSO), NaBr, 12 wt% NaClO solution, 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO, 98%), ethanol, dimethyl formamide (DMF), glutaraldehyde (GA, 50%), dodecyl trimethyl ammonium bromide (DTAB) and other chemicals were of laboratory grade (Aladdin Chemical Regents Co., Ltd., China) and used as received without further purification.

Table 1
Surface tension test results of different solutions.

Solutions	Concentration (w/v%)	Surface tension (mN/m)
DTAB	0.05	22.95
	0.10	21.97
	0.125	17.35
	0.15	17.55
JCNs	.005	63.77
	0.10	62.56
	0.15	52.17
DTAB + JCNs	0.05 + 0.05	37.12
	0.05 + 0.10	36.81
	0.05 + 0.15	35.18

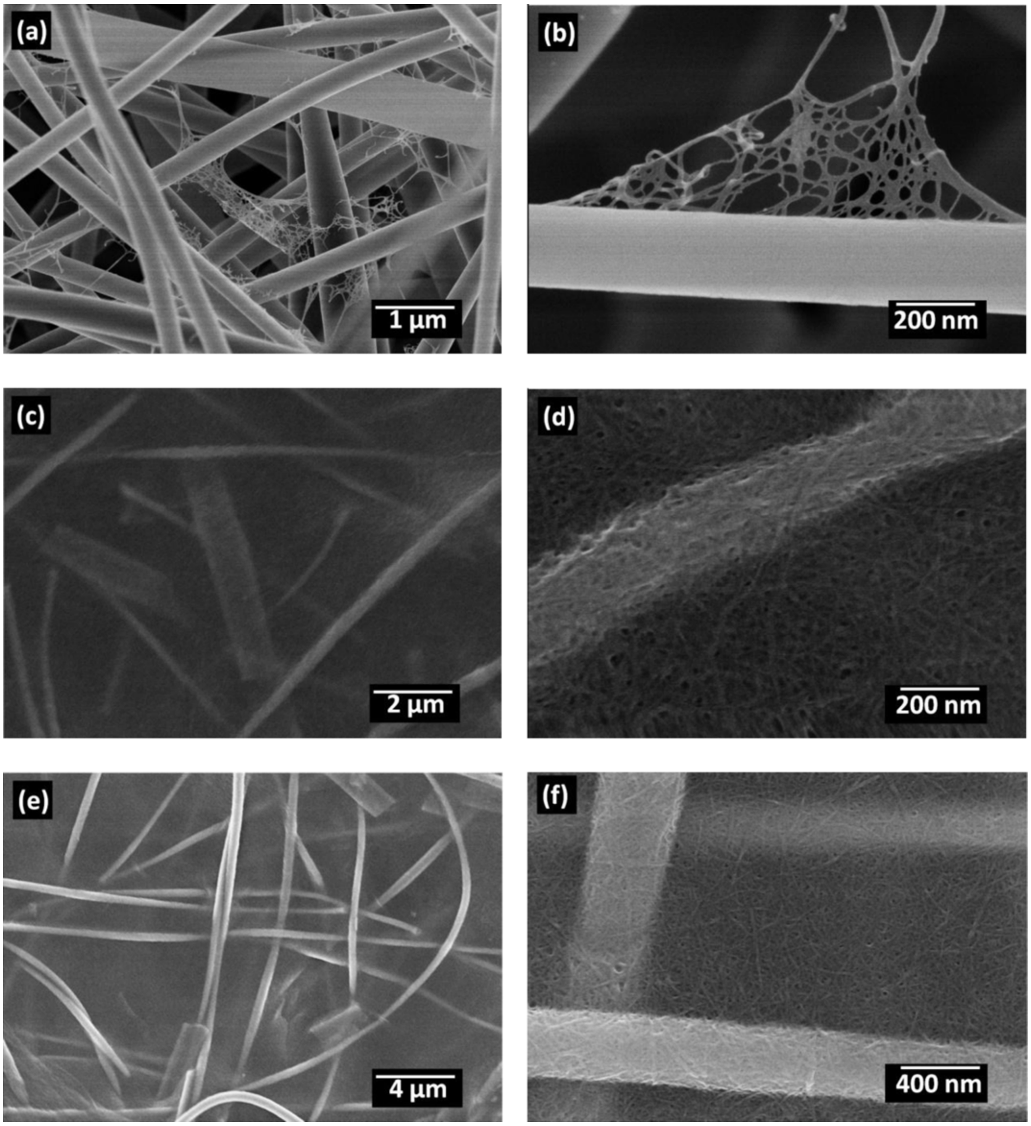

Fig. 2. FE-SEM images for the JCNs/silica nanofibrous membranes with different contents of JCNs suspension: (a and b) 0.05 w/v%, (c and d) 0.10 w/v%, and (e and f) 0.15 w/v%.

2.2. *Preparation of jute cellulose nanowhiskers(JCNs) suspension*

Preparation of jute cellulose nanowhiskers (JCNs) suspension was performed according to the procedure described elsewhere (Cao et al., 2012). The jute (10 g) was dispersed in the solution with water (190 g), NaBr (0.20 g) and TEMPO (0.02 g). The reaction was started by the addition of 12 wt% NaClO solution (18 g) under stirring. The pH was kept at 10–10.5, monitored with a pH meter, by adjusting with 2 wt% NaOH aqueous solution. The reaction was stopped by adding 5 mL ethanol while no NaOH consumption, followed by stirring for another 20 min. The final product was washed with deionized water by successive centrifugations (5000 rpm for 10 min) until neutral. Oxidized cellulose slurry (1.0 g) was dispersed in 100 g of water and sonicated for 5 min at 13,000 rpm with an IKA T25 homogenizer (IKA Works, Shanghai, China). The suspension was centrifuged at 5000 rpm for 30 min, and the recovered supernatant became the JCNs aqueous suspension.

2.3. *Preparation of ES nanofibrous membranes*

6 wt% PAN electrospinning solutions were prepared by dissolving in DMF at 60 °C with vigorous stirring for 6 h. 10 wt% PVA electrospinning solutions were prepared by dissolving in pure water at 80 °C with vigorous stirring for 6 h. For silica ES membranes, silica gels with the molar composition of TEOS:H_3PO_4:H_2O = 1:0.01:11 were prepared by hydrolysis and polycondensation by dropwise addition of H_3PO_4 into TEOS with stirring at room temperature for 6 h. Then 10 g of 10 wt% PVA solutions were added slowly into 10 g of silica gel and stirred for another 4 h. Thus, viscous precursor solutions containing PVA, used as the electrospinning solutions, were obtained. To get the pure silica nanofibrous membranes, the ES fibrous membranes were calcined at 800 °C with a temperature increase rate of 5 °C min^{-1} in air, then cooled down to room temperature, which was reported by our previous work (Zhao et al., 2011). All the PVA, PAN and silica nanofibrous membranes were prepared at 20 kV in a relative humidity of 40% at 24 °C at a feed rate of 1 mL/h and with a constant tip to collector distance of 18 cm using DXES-1 spinning equipment (Shanghai Oriental Flying Nanotechnology Co., Ltd., China).

2.4. *Preparation of JCNs/ES nanofibrous membrane*

The ES nanofibrous membranes were dipped into the dispersions of DTAB (0.05, 0.10, and 0.15 w/v%) and jute cellulose

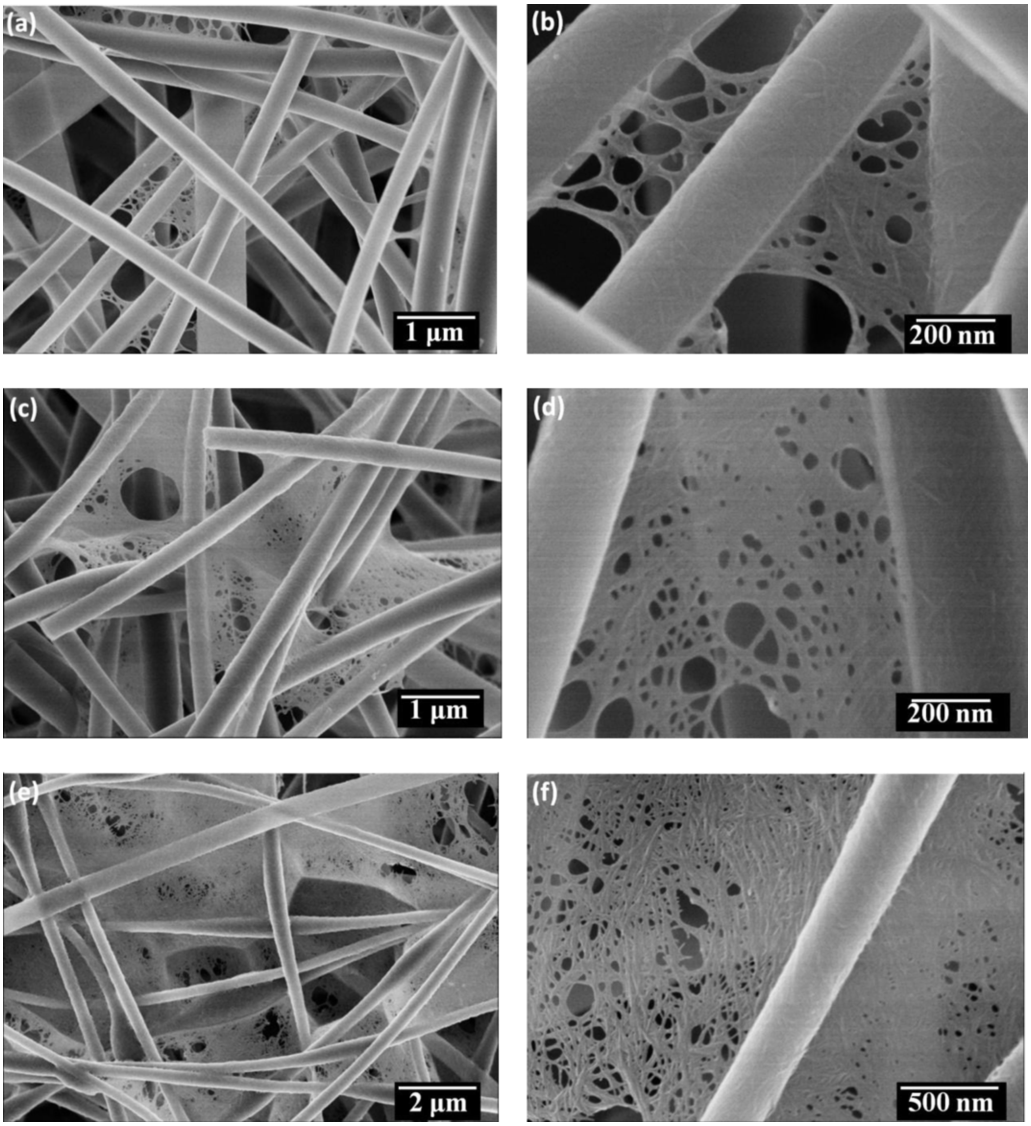

Fig. 3. FE-SEM images for the JCNs/silica nanofibrous membranes with different surfactant content: (a and b) 0.05 w/v%, (c and d) 0.10 w/v%, and (e and f) 0.15 w/v%.

nanowhiskers (0.05, 0.10, and 0.15 w/v%) in a glass bottle. The bottle containing dispersions and membranes was then placed under reduced pressure for 5 min using a vacuum pump to remove air bubbles present in the dispersions. The membranes were vertically removed from the dispersions in the bottle and excess dispersions carried over in the lower part of the membranes were removed by filter paper. The wet membranes were dried under different conditions, such as air dry, vacuum without heating and vacuum heating at 120 and 150 °C. Specially, the PVA nanofibrous membrane was chemical crosslinked by 0.2 M GA/ethanol for 2 days before use as reported by (Wang & Hsieh, 2010).

2.5. Characterization

2.5.1. Surface tension test

The surface tensions of cellulose nanowhiskers, DTAB solutions, and their mixtures were test by a surface tension tester (QBZY, Fangrui Instrument Co. Ltd., Shanghai, China). Five tests for each sample were done to get an average value under room temperature and relative humidity of 50%.

2.5.2. Field-emission scanning electron microraph (FE-SEM)

The top morphologies of different ES nanofibrous composite membranes were examined using a field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi Co. Ltd., Japan).

3. Results and discussion

3.1. Surface tension test

From the point of view of molecular force, the molecules in fluid are constantly in a Brownian motion. However, inside liquid, there is mutual attraction (including repulsive force) between the molecules of fluid. Therefore, the resultant molecular force on the molecules in the bulk of liquid is zero. The mutual attraction between the molecules of the same kind of substance is defined as cohesion. Liquid is prone to gradually narrow liquid surface area. Surface tension is referred to the force on the liquid surface which makes the liquid level contracted into a minimum area (Tyson & Miller, 1977). The surface tension of the solutions directly influences the distribution of cellulose nanowhiskers on the nanofibrous membranes when it dried.

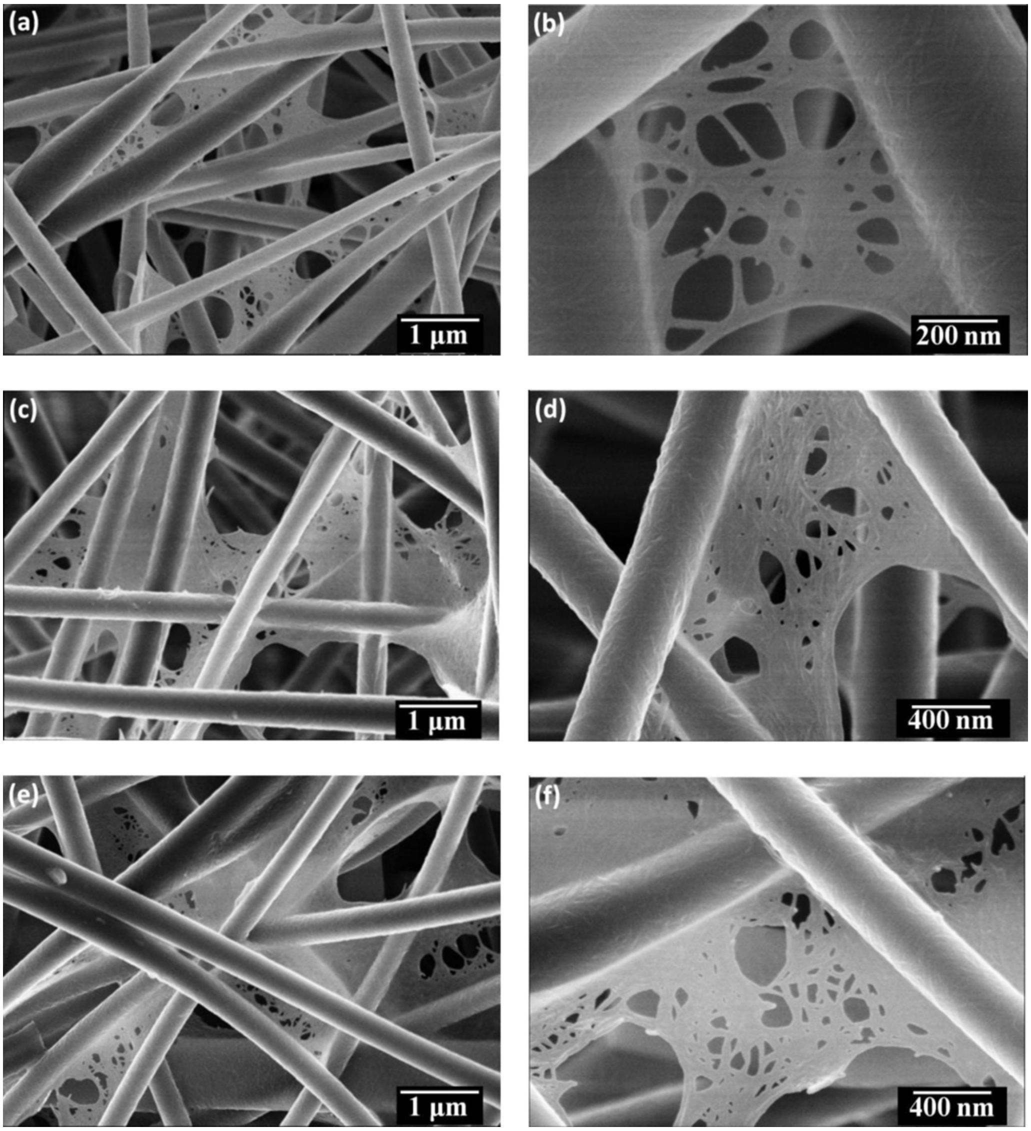

Fig. 4. FE-SEM images for the JCNs/silica nanofibrous membrane under different drying conditions: (a and b) atmosphere, (c and d) vacuum without heating, and (e and f) 150 °C in vacuum.

Table 1 lists the surface tension test results of different solutions. We could see that the surface tensions of the JCNs suspensions, DTAB solutions, and their mixture are smaller than that of pure water (72.8 mN/m) (Jan & Helmut, 2004), and the introduction of DTAB sharply decreases the surface tension of cellulose nanowhiskers suspensions. With the increasing of concentration of cellulose nanowhiskers and DTAB, the surface tension of both decrease. This could be interpreted by the surface tension of solutions affected by solute. Gibbs equation suggested that,

$$\Gamma = -\left(\frac{d\sigma}{dc}\right) \times \frac{c}{RT} \tag{1}$$

where Γ is the surface excess, σ is the surface tension, T is the thermodynamic temperature, R is the gas content, c is the concentration of solutions. When $(d\sigma/dc) < 0$, $\Gamma > 0$, which was defined as surface active substance (Rotenberg, Boruvka, & Neumann, 1983). Because of its decreasing the surface tension of solutions, it was called surfactant.

3.2. Morphology of nanoporous networks on different nanofibrous membranes

Fig. 1 shows the FE-SEM images of the nanoporous JCNs networks on different supports of nanofibrous membranes including PAN, chemical crosslinked PVA, and silica. It could be seen that two dimensional (2D) ultrathin nanoporous networks based on cellulose nanowhiskers with diameter less than 10 nm were fabricated on the PAN, PVA, and silica nanofibrous membrane supports. One thing should be pointed out that all the selected supports are super-hydrophilic. It could also be seen that there are cellulose nanowhiskers not only between the nanofibers, but also on the surface of PAN (Fig. 1a and b) and PVA nanofibers (Fig. 1c and d), which make the fiber surface rough. However, for the silica nanofibrous membrane, we could only see the cellulose nanowhiskers between the silica nanofibers but not on the silica nanofibers, where the networks have the largest coverage area and the silica nanofibers surface is still smooth (Fig. 1e and f). During the following experiment, we choose silica nanofibers as the support to discuss the effect factors of the formation of the nanoporous networks.

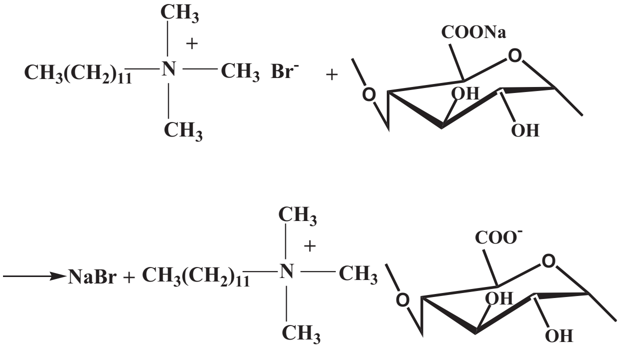

Fig. 5. Reaction between DTAB and TEMPO oxidized cellulose.

3.3. *Effect of concentrations of JCNs suspensions*

Fig. 2 shows the FE-SEM images for the JCNs/silica nanofibrous membrane with different contents of JCNs suspensions. 2 mL of 0.05 w/v% DTAB solutions were slowly added into 8 mL of three different contents of JCNs suspensions, 0.05, 0.10, and 0.15 w/v%, which were slowly stirred at 150 rpm for 5 min. The silica fibrous JCNs composite membranes were prepared by simple immersing-drying process. It could be seen that when the content of the JCNs suspension was 0.05 w/v%, there were spider web like networks formed by jute cellulose nanowhiskers with widths of less than 10 nm and their bundles between the silica fibers (Fig. 2a and b). For the content of 0.10 w/v% JCNs suspension samples, both the silica fibers and the voids between them were covered by dense cellulose nanowhiskers membranes (Fig. 2c and d). As the increasing of the JCNs suspensions contents, the JCNs formed more dense membranes by themselves (Fig. 2e and f). During the following experiment, the content of JCNs suspension was set as 0.05 w/v%.

3.4. *Effect of the addition content of DTAB*

Fig. 3 shows the FE-SEM images of the JCNs/silica nanofibrous membranes with different surfactant contents. While keeping the content of JCNs suspension constant (0.05 w/v%), as the increasing of concentration of DTAB, the coverage rate of JCNs networks increased, and the network structure packed more densely. That is to say, we could adjust it according to the practical desire.

3.5. *Effect of the drying conditions*

Fig. 4 shows the FE-SEM images for the JCNs/silica nanofibrous membranes under different drying conditions. Keeping the jute cellulose nanowhiskers suspension content of 0.05 w/v% and the DTAB concentration of 0.05 w/v%, the samples dried in air exhibited evenly distributed networks, while the coverage area for vacuum drying samples increased as the temperature increased.

3.6. *Mechanism of nanoporous networks formation*

TEMPO oxidized cellulose nanowhiskers have high surface free energy for numerous carboxyl and hydroxy groups present on its surface (Hirota, Furihata, Saito, Kawada, & Isogai, 2010; Isogai, Saito, & Fukuzumi, 2011; Okita, Saito, & Isogai, 2010; Saito, Shibata, Isogai, Suguri, & Sumikwa, 2005). Therefore, during the direct drying of the JCNs aqueous suspensions, the oxidized cellulose nanowhiskers would highly aggregate to obtain transparent films with good gas barrier properties (Fukuzumi, Saito, Iwata, Kumamoto, & Isogai, 2009). Hydrophobic groups were introduced into its surface to decrease the polarity and surface free energy of JCNs and finally to prevent its rapid aggregation during drying. As shown in Fig. 5, the reaction between DTAB and JCNs converted the carboxyl group of TEMPO oxidized cellulose to the hydrophobic group. The JCNs/DTAB suspensions maintained a stable dispersion without gelation or sedimentation for hours in the atmosphere environment. If DTAB completely reacted with equimolar to carboxyl group of TEMPO oxidized cellulose, there would be NaBr ions or molecules at a level equimolar to the carboxyl group of TEMPO oxidized cellulose (Junji, Toshihiko, Saito, & Isogai, 2012). If only part of DTAB reacted with JCNs, the unbound DTAB and NaBr would coexist, which would influence the formation of nanoporous structures. This should be studied further in the future.

4. Conclusions

In summary, JCNs nanoporous networks, similar in appearance to spider webs, were prepared by simple immersing-drying of JCNs/DTAB dispersions using PAN, crosslinked PVA, and silica electrospun nanofibrous membrane supports containing submicrometer-sized pores. The porous JCNs networks were composed of a mixture of single JCNs with widths smaller than 10 nm and JCNs bundles. Additionally, the versatile nanoporous composites would be particularly useful for ultrafiltration applications. We believe that the method described here with much lower energy consumption could be easily extended to provide a route to produce high performance filter from cellulose nanowhiskers.

Acknowledgements

This work is supported by the National Basic Research Program of China (973 Program, 2011CB606103 and 2012CB525005), the National Natural Science Foundation of China (No. 51173022, U1232116 and 51273038), the Shanghai Nano Special Projects (11nm0502900), the Innovation Program of Shanghai Municipal Education Commission (11ZZ59), the “Dawn” Program of Shanghai Education Commission (10SG32), the Huo Yingdong Foundation (131070), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education of China, the Program for New Century Talents of the University in China, and the Fundamental Research Funds for the Central Universities.

References

Burger, C., Hsiao, B. S., & Chu, B. (2006). Nanofibrous materials and their applications. *Annual Review of Materials Research*, *36*, 333–368.

Cao, X., Ding, B., Yu, J., & Al-Deyab, S. S. (2012). Cellulose nanowhiskers extracted from TEMPO-oxidized jute fibers. *Carbohydrate Polymers*, *90*(2), 1075–1080.

Cao, X., Ding, B., Yu, J., & Al-Deyab, S. S. (2013). In situ growth of silver nanoparticles on TEMPO-oxidized jute fibers by microwave heating. *Carbohydrate Polymers*, *92*(1), 571–576.

Ding, B., Wang, M., Wang, X., Yu, J., & Sun, G. (2010). Electrospun nanomaterials for ultrasensitive sensors. *Materials Today*, *13*(11), 16–27.

Fukuzumi, H., Saito, T., Iwata, T., Kumamoto, Y., & Isogai, A. (2009). Transparent and high gas barrier films of cellulose nanofibers prepared by TEMPO-mediated oxidation. *Biomacromolecules*, *10*(1), 162–165.

Hirota, M., Furihata, K., Saito, T., Kawada, T., & Isogai, A. (2010). Glucose/glucuronic acid alternating co-polysaccharides prepared from TEMPO-oxidized native celluloses by surface peeling. *Angewandte Chemie International Edition*, *49*(42), 7670–7672.

Hu, J., Wang, X., Ding, B., Lin, J., Yu, J., & Sun, G. (2011). One-step electro-spinning/netting technique for controllably preparing polyurethane nano-fiber/net. *Macromolecular Rapid Communications*, *32*(21), 1683–1734.

Isogai, A., Saito, T., & Fukuzumi, H. (2011). TEMPO-oxidized cellulose nanofibers. *Nanoscale*, *3*, 71–85.

Jan, R., & Helmut, C. (2004). Superstructures of temporarily stabilized nanocrystalline $CaCO_3$ particles: Morphological control via water surface tension variation. *Langmuir*, *20*(3), 991–996.

Junji, N., Toshihiko, S., Saito, T., & Isogai, A. (2012). Nanoporous networks prepared by simple air drying of aqueous TEMPO-oxidized cellulose nanofibril dispersions. *Biomacromolecules*, *13*(3), 943–946.

Kristin, S., & Per, S. (2009). Strength and barrier properties of MFC films. *Cellulose*, *16*(1), 75–85.

Ma, H., Burger, C., Hsiao, B. S., & Chu, B. (2011). Ultrafine polysaccharide nanofibrous membranes for water purification. *Biomacromolecules*, *12*(4), 970–976.

Okita, Y., Saito, T., & Isogai, A. (2010). Entire surface oxidation of various cellulose microfibrils by TEMPO-mediated oxidation. *Biomacromolecules*, *11*(6), 1696–1700.

Rotenberg, Y., Boruvka, L., & Neumann, A. W. (1983). Determination of surfacetension and contact angle from the shapes of axisymmetric fluid interfaces. *Journal of Colloid and Interface Science*, *93*(1), 169–183.

Saito, T., Nishiyama, Y., Putaux, J. L., Vignon, M., & Isogai, A. (2006). Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules*, *7*(6), 1687–1691.

Saito, T., Shibata, I., Isogai, A., Suguri, N., & Sumikwa, N. (2005). Distribution of carboxylate groups introduced into cotton linters by the TEMPO-mediated oxidation. *Carbohydrate Polymers*, *61*(4), 414–419.

Saito, T., Uematsu, T., Kimura, S., Enomae, T., & Isogai, A. (2011). Self-aligned integration of native cellulose nanofibrils towards producing diverse bulk materials. *Soft Matter*, *7*, 8804–8809.

Svagan, A. J., Samir, M. A. S. A., & Berglund, L. A. (2008). Biomimetic foams of high mechanical performance based on nanostructured cell walls reinforced by native cellulose nanofibrils. *Advanced Materials*, *20*(7), 1263–1269.

Svensson, A., Nicklasson, E., Harrah, T., Panilaitis, B., Kaplan, D. L., Brittberg, M., et al. (2005). Bacterial cellulose as a potential scaffold for tissue engineering of cartilage. *Biomaterials*, *26*(4), 419–431.

Tyson, W. R., & Miller, W. A. (1977). Surface free energies of solid metals: Estimation from liquid surface tension measurements. *Surface Science*, *62*(1), 267–276.

Wagberg, L., Decher, G., Norgren, M., Lindstrom, T., Ankerfors, M., & Axnas, K. (2008). The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes. *Langmuir*, *24*(3), 784–795.

Wang, N., Wang, X., Ding, B., Yu, J., & Sun, G. (2012). Tunable fabrication of three-dimensional polyamide-66 nano-fiber/nets for high efficiency fine particulate filtration. *Journal of Materials Chemistry*, *22*(4), 1445–1452.

Wang, X., Ding, B., Yu, J., & Wang, M. (2011). Engineering biomimetic superhydrophobic surfaces of electrospun nanomaterials. *Nano Today*, *6*, 510–530.

Wang, X., Wang, J., Si, Y., Ding, B., Yu, J., & Sun, G. Polyaniline functionalized polyamide 6 nano-fiber/net as quartz crystal microbalance sensing layers for detection of trace hydrogen chloride gas. Nanoscale, in press

Wang, Y., & Hsieh, Y. L. (2010). Crosslinking of polyvinyl alcohol (PVA) fibrous membranes with glutaraldehyde and PEG diacylchloride. *Journal of Applied Polymer Science*, *6*, 3249–3255.

Zhao, F., Wang, X., Ding, B., Lin, J., Si, Y., Yu, J., et al. (2011). Nanoparticles decorated fibrous silica membranes exhibiting biomimetic superhydrophobicity and highly flexible properties. *RSC Advances*, *1*(8), 1482–1488.