Oriented Zeolite AFI Membranes: Anti-Water and Quick Blood-Clot

Wenzhao Liang\textsuperscript{1}, Shanshan Yu\textsuperscript{3}, Kangjian Tang\textsuperscript{4} and Junzhi Liu\textsuperscript{2,*}

\textsuperscript{1}Department of Neurology, China-Japan Union Hospital of Jilin University, Changchun 130012, P.R. China
\textsuperscript{2}Quality control Office, China-Japan Union Hospital of Jilin University, Changchun 130012, P.R. China
\textsuperscript{3}Department of Anesthesiology, China-Japan Union Hospital of Jilin University, Changchun 130012, P.R. China
\textsuperscript{4}Shanghai Research Institute of Petrochemical Technology, SINOPEC, Shanghai 201208, China

*Corresponding author e-mail: 34174911@qq.com

Abstract. Hemorrhagic death is one of the leading preventable causes of mortality in traumatic injury. Considerable efforts have been made to explore the effective hemostatic agents that can be applied directly to the bleeding wound. In the present research, FE-SEM images, water absorption and human blood clotting experiments have been used to study the membrane of aluminophosphate molecular sieve AFI-5, which showed that its packed surface has excellent properties of super amphiphilicity, suggesting that AFI-5 may be useful in accelerating blood coagulation and shortening the clot formation time as an inexpensive human blood clotting agent like the zeolite-containing QuikClot, but with a thin surface coverage.

1. Introduction

Zeolites and zeolite-like molecular sieves have been used as ion exchangers, absorption media, and catalysts for decades [1-4]. Recently these solids have been developed into other functional materials such as MRI contrast agents and are being explored in numerous advanced material applications [5-6]. Of interest to this work, a zeolite-based blood clotting agent called QuikClot was approved for the uncontrolled life-threatening hemorrhage by the Food and Drug Administration (FDA) in 2002 [7]. QuikClot is a dehydrated powder comprised of a zeolite with the FAU topology and other inorganic solids [8-9]. It is used for traumatic wound treatments and can stop high-volume blood loss in large wounds [10-13]. The dried sterile powder is poured directly on the wound site where it rapidly absorbs water [14]. A known side effect of the highly exothermic absorption is a local rise in temperature that can cause pain and the burning of tissue. The possible cauterizing effects of the heat released are not thought to be significant [15]. Efforts to decrease the heat released have involved the use of a wide variety of other metal oxides that did not include aluminophosphates and partially, rather than fully, dehydrating the zeolite [16-17]. Since the absorption of water into microporous materials will always be an exothermic process with a minimum energy corresponding to the heat of condensation of water, one method for decreasing the energy release is to use a solid that minimizes its interaction energy...
with water. For crystalline microporous materials, pure-silica solids are hydrophobic and thus do not readily absorb water. Aluminophosphate structures do absorb water with energies just slightly above the heat of liquefaction [18]. The aluminophosphate molecular sieve (AFI) may be of any aluminophosphate structure. Preferred structures include AIPO4-5 and VPI-5[19-20]. Here, we show that the membrane of aluminophosphate molecular sieves, which consist of AIPO4-5, can be used to clot blood like QuikClot with a thin coverage.

2. Experimental

2.1. Materials:
Phosphoric acid (85%), tri-ethylamine (99.5%), butanol (99.4%), toluene (99.5%), aluminum tri-isopropoxide (99.99%) and hydrofluoric acid (48%) were purchased from Beijing chemical plant. Cetylpyridinium chloride (CPC, 98%) was from Alfa Aesar. 1H, 1H, 2H, 2H-Tridecafluoro-n-octyltriethoxysilane was from Guide Chem of China. All materials were used as received.

2.2. Preparation of oriented AFI membranes
AFI membranes were prepared in a reverse microemulsion system (according to the literature) by hydrothermal method [17].

2.3. Characterization of AFI membranes:
X-ray diffraction experiments: X-ray powder diffraction (XRD) analyses of the products were carried out on a Siemens D5005 X-ray diffract meter with Cu Kα radiation (λ = 1.5418 Å).

SEM measurements: The surfaces of synthesised membranes were investigated by a field-emission scanning electron microscopy (FE-SEM: JEOS JSM 6700F; V=5kV, WD=7mm).

Wetting property analysis: The water contact angle was measured on FTÅ 200 Series W/R S232 control at ambient temperature. Camera Video and Frame Grabber were carried on V4 and FG4 Mutech MV-510 JAI M30 Camera.

3. Results and Discussion
SEM images, as shown in Fig 1, revealed the morphologies of AFI crystals with different introducing amount of styrene. Fig 1a showed synthesis with a weight ratio of micro emulsion to styrene (Wm/Ws) as 14.3. It revealed that the crystal had hexagonal slice morphology with the area of around 30 µm² and thickness of 2 µm. Fig 1b showed the synthesis with Wm/Ws as 5.73, the crystals changed to form bigger blocks. Fig 1c showed the synthesis with Wm/Ws as 4.78. Stick-shaped crystals and big blocks piled up on the substrate to form conical and chaotic patterns. Fig 1d showed the synthesis with Wm/Ws as 3.44, the crystal changed to form round brushes with higher aspect ratio than sticks seen in Fig 1c. The differences of these morphologies were then investigated by XRD. Fig 1e to 1g showed the XRD patterns corresponding to Fig .1a~d. Fig 1a revealed that crystals are zeolite AFI, the structure could be indexed to JACDS 10-0044. Fig 1e and 1f revealed the co-existence of AFI and Berlinite structure (JACDS 10-0423). Fig 1e revealed the crystals structure were AFI as Fig 1f, but with different morphology. Obviously, the XRD patterns with characteristic reflection peaks of zeolite AFI for all the samples showed strongly enhanced intensity of the (002) peak at the Bragg angle of 2θ of around 21°. This enhanced intensity confirmed the AFI crystals grow with their one-dimensional 12-MR channels (diameter: 0.73 nm) along the c-axis. Consequently, the morphology of AFI could be controlled via such polymer/micro emulsion approach. It is inferred there would exist an interesting structure competition.

The oriented AFI membrane was prepared based on the formula as ratio of microemulsion to styrene (Wm/Ws) as 3.44 on AAO. Fig 1f showed the full orientation of stick crystals. The wetting property of the AFI film was studied by a contact angle instrument. When a water or a heptane droplet (drop weight 4 mg) was placed on the surface, Both the liquid was absorbed into the AFI microstructure membrane in less than 0.55s, as shown in Figure 2a and 2b, This suggested that the
surface containing oriented AFI microstructures, exhibited excellent superhydrophilic and superoleophilic property, meaning superamphiphilicity. The surface of AFI membrane became superhydrophobic and ultraoleophilic after surface modification with fluoroalkylsilane. The contact angle on this surface was about 152° and the tilt angle of the surface was less than 3°, as shown in Figure 2c and 2d, suggesting that the surface changes from superhydrophilicity to superhydrophobicity. Significantly, the heptane droplet is absorbed into the microstructure film just less than 0.04s, as shown in Fig 2e, which exhibited excellent ultraoleophilicity.

The equation transformed from Cassie–Baxter law[21] could help to understand the unique wetting from superhydrophilic to superhydrophobic behavior:

\[ \cos \theta_r = f \cos \theta_s - (1-f) \]  

In eqn 1, \( \theta_r \) is the contact angle of the liquid on the rough surface, \( \theta_s \) is the contact angle of the liquid on the smooth surface having the same chemistry as the rough surface, \( f \) is the fraction of liquid-solid interface area, \( (1-f) \) is the remaining fraction of the drop base. As is known, the AlPO\(_4\)-5, with high surface energy, is classic hydrophilic material and the as-prepared oriented zeolite membranes can be considered as a porous rough surface [22-23], which lead a super hydrophilic behavior, when the \( (1-f) \) would be very small, \( f \approx 1 \). With a surface modification, the membrane was covered by a self-assembled monolayer of fluoroalkylsilane. The modified surface is mostly occupied by air, \( (1-f) \) would be dominant, \( (1-f) \approx 1 \).

Aiming the application of Quick-clot, one membrane with superamphiphilicity on one side and super hydrophobicity on other side (covered by fluoroalkylsilane) was used to test blood adsorption and anti-dropping water. Fig 2f showed one freshly extracted human blood droplet on the AFI covered superhydrophilic surface. As seen, the blood droplet was imbibited into the membrane as fast as 0.4s. Moreover, the other superhydrophobic side showed a strong elasticity to water. Fig 2g showed the observation of a dynamical characteristic of such a water-repellent surface. The rebound is possibly made by the small dissipation as the drop impacts the solid: because of the high contact angle, viscous dissipation close to the moving contact line (which usually is the primary cause of viscous loss) nearly becomes negligible, which keeps its contact angle very high, allowing it to store its kinetic energy in surface deformation, and thus to bounce back. This character had some practical applications, such as on “Band Aid” with its anti-water while bathing etc.

4. Conclusion

In conclusion, the present work demonstrates a microemulsion hydrothermal synthesis method to prepare AFI membranes on porous substrates. The relation of the surface microstructures with their wetting properties is observed and discussed. Our results demonstrated that packed surface has excellent properties of super amphiphilicity; and super hydrophobicity, as to be used on anti-water surface. Such membrane materials could be useful as inexpensive, anti-water, human blood clotting agents.
Figure 1. (a-d) SEM images of asprepared AFI crystals; (e) X-ray diffraction patterns of asprepared AFI crystals; (f) SEM images of oriented AFI membrane (Inset: the magnified view).

Figure 2. Behavior of a water and a heptane droplet on AFI film before and after surface modification.

Before surface modification: (a), (b) The process of water and heptane droplet is absorbed into the AFI microstructure film, respectively. After surface modification: (c) Shape of a water droplet on the surface with a CA of 162o (drop weight 4 mg) (d) sliding angle is less than 3o. (e) The process of a heptane droplet is absorbed into the AFI microstructure film within less 0.04s; (f) A blood droplet was imbibed into one superhydrophilic surface within 0.4 second. (g) A water droplet fell from 4cm to the other superhydrophobic surface and bounces off (Snap: fame per 1/60 second). Inset: Shape of the water droplet on the surface at stable state after bouncing with a CA over 150o.

Acknowledgments
This work was financially supported by NSFC81700393, 2016Q017, JJKH20170856K fund.

References
[1] X. He, D. Antonelli, Angew. Chem. Int. Ed. Engl. 41 (2002) 215–229.
[2] V.F. Kispersky, A.J. Kropf, F.H. Ribeiro, J.T. Miller, Phys. Chem. Chem. Phys. Pccp 14 (2012) 2229–2238.
[3] T.C. Keller, Chem. Sci. 5 (2014) 677–684.
[4] M.J. Stephenson, M.P. Attfield, S.M. Holmes, R.A.W. Dryfe, J. Solid State Electrochem. (2015) 1–8.
[5] M.E. Davis, Nature 417 (2002) 813–821.
[6] J.A. Peters, K. Djianashvili, Eur. J. Inorg. Chem. 2012 (2012) 1961–1974.
[7] J. Li, W. Cao, X. Lv, L. Jiang, Y. Li, W. Li, S. Chen, X. Li, Acta Pharmacol. Sin. 34 (2013) 367–372.
[8] A.E. Pusateri, A.V. Delgado, D.E. Jr, R.S. Martinez, J.B. Holcomb, K.L. Ryan, J. Trauma 57 (2004) 555–562.
[9] F.L. Wright, H.T. Hua, G. Velmahos, D. Thoman, D. Demetriades, P.M. Rhee, J. Trauma 56 (2004) 205–208.
[10] J. Li, W. Yan, L. Jing, L. Xueyong, L. Yuejun, L. Wangzhou, C. Shaozong, J. Trauma 66 (2009) 612–620.
[11] H.B. Alam, Z. Chen, A. Jaskille, R.I. Querol, E. Koustova, R. Inocencio, R. Conran, A. Seufert, N. Ariaban, K. Toruno, J. Trauma Acute Care Surg. 56 (2004) 974–983.
[12] P. Rhee, C. Brown, M. Martin, A. Salim, D. Plurad, D. Green, L. Chambers, D. Demetriades, G. Velmahos, H. Alam, J. Trauma-Injury, Infect. Crit. Care 64 (2008) 1093–1099.
[13] M.H. Motamedi, M. Sagafinia, Prehospital Disaster Med. Off. J. Natl. Assoc. EMS Physicians World Assoc. Emerg. Disaster Med. Assoc. with Acute Care Found. 26 (2011).
[14] Francis Hursey X, F.J. Dechene, (1989). U.S. Patent No. 19894822349.
[15] J.K. Wright, J. Kalns, E.A. Wolf, F. Traweek, S. Schwarz, C.K. Loeffler, W. Snyder, Y.L. Jr, J. Eggers, J. Trauma 57 (2004) 224–230.
[16] Francis Hursey X, A. Wu, S.L. Suib, S.L. Bushmich, J. Liu, B. Hincapie, (2003). U.S. Patent No. 20030133990.
[17] Francis Hursey X, (2005). U.S. Patent No.20050058721.
[18] K. Tsutsumi, K. Mizoe, K. Chubachi, Colloid Polym. Sci. 277 (1999) 83–88.
[19] A. Hassanvand, M. Asghari, Int. J. Nano Dimens. 2 (2011) 147–149.
[20] X. Yin, Z. Li, S. Wang, N. Chu, J. Yang, J. Wang, Microporous Mesoporous Mater. 201 (2015) 247–257.
[21] W. Choi, A. Tuteja, J.M. Mabry, R.E. Cohen, G.H. Mckinley, J. Colloid Interface Sci. 339 (2009) 208–216.
[22] C. Ji, Y. Tian, Y. Li, Y.S. Lin, Microporous Mesoporous Mater. 186 (2014) 80–83.
[23] G. Bellussi, R. Millini, E. Montanari, A. Carati, C. Rizzo, P.W. Jr, G. Cruciani, A.A. De, L. Bonoldi, S. Zanardi, Chem. Commun. 48 (2012) 7356–7358.