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Zwitterionic Polymer Grafted Superhydrophilic and Superoleophobic Silk Fabrics for Anti-oil Applications

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Abstract: In this study, we synthesized a highly anti-oil fabric membrane by surface grafting of zwitterionic poly (sulfobetaine methacrylate) (PSBMA) onto the fabric surface. The fabric membrane was first enzymatically modified to create more reactive amine groups on the surface. A surface-initiated atom-transfer radical polymerization (SI-ATRP) reaction was then performed to modify the fabric membrane surface with a dense PSBMA brush layer. Surface characterization indicated that the brush grafted fabric membrane exhibited increased surface roughness and improved superhydrophilicity. The PSBMA modified silk fabrics show very large contact angle for oil-droplets in water, and have excellent oil resistance in air and in water-oil mixtures.

Large amounts of oily wastewater is produced in various industries such as mining, food, textiles, and petrochemical industry, which has caused a serious problem to the environment.^[1] Besides that, the resulting oil pollution on the marine and shipping equipment also causes great economic losses. Great efforts have paid to prevent the adhesion of oil on the surface. Thus, the development of anti-oil material is critical to the sustainability of human society.^[2] And there are widespread potential applications of materials with underwater superoleophobicity, such as antifouling, self-cleaning,

antifogging and oil/water separation.^[3-5]

Commonly developed oil-resistant materials are obtained by adjusting the wettability to be superoleophobic, including underwater superoleophobic (superhydrophilic) whose oil contact angle underwater (OCA) is $>150^\circ$ at the oil/water/solid interface.^[6] Such superoleophobicity can be obtained by using the synergistic effects of surface energy and roughness.^[7] Previous studies showed that the hydrophilicity of surfaces depends on the surface morphology and assembly of hydrophilic organic, inorganic or hybrid materials on the surfaces. TiO_2 , SiO_2 and Al_2O_3 are often introduced into the surface or interior of substrate to realize superhydrophilicity.^[8-10] However, the inorganic component is mostly dispersed or embedded in the polymer matrix, which decreases the efficiency of the modification. Surfaces with such micro/nano-features are susceptible to damage from abrasion and corrosion in water, so the applications of such materials is often limited.^[11]

Surfaces modification with hydrophilic polymers, such as polydopamine (PDA), poly(acrylic acid) (PAA), polyethylene glycol (PEG) and polyacrylamide (PAM), is a widely used method to adjust the hydrophilicity of surfaces.^[12-15] Jin *et al.* fabricated a superhydrophilic PAA grafted PVDF filter membrane with a hierarchical micro/nanoscale structure by a salt-induced phase-inversion approach, which can be used for anti-oil fouling.^[14] Among all the approaches, surface coating of PDA is a very common strategy, and the PDA can be as a versatile immobilization platform to covalently anchor another layer that can be a grafted superhydrophilic polymer chains or self-assembled monolayer.^[16, 17]

In recent years, researches show that zwitterionic polymers, such as poly(sulfobetaine 2-vinylpyridine) (SB2VP), poly(carboxybetaine methacrylate) (PCBMA), poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) and poly(sulfobetaine methacrylate) (PSBMA), can function as an excellent class of materials for surface modification of anti-oil membranes.^[18-24] The zwitterionic polymers carry functional groups like carboxybetaine, sulfobetaine and phosphobetaine etc., which have both negatively and positively charge in the same monomer.^[25] The

strong polarity give rises to a hydration layer around the zwitterionic polymer chains,^[26, 27] which can prevent the adsorption of oil droplets onto the polymer surfaces.^[28] Studies have reported that copolymer hydrogels prepared by poly(ethylene glycol)diacrylate (PEGDA) and zwitterionic monomer, such as carboxybetaine methacrylate (CBMA) and sulfobetaine methacrylate (SBMA), demonstrate better hydrophilicity than those PEGDA.^[29, 30] Most of the zwitterionic materials are coated onto the surface of various substrates to enhance the hydrophilicity.^[31-33] It is reported that coatings by the simultaneous deposition of polydopamine (PDA) with PMPC can enhance the biocompatibility, hydrophilicity, and fouling resistance of the silicon wafers.^[31] Zhu *et al.* reported the fabrication of a nano-sized zwitterionic hydrogels grafted onto a poly(vinylidene fluoride) (PVDF) microfiltration filter membrane (ZNG-g-PVDF), which showed superoleophobicity in water with nearly zero oil adhesion and excellent durability in solution.^[34]

Zwitterionic polymers surfaces can also be created using a ‘graft-from’ approach,^[35] Elimelech *et al.* fabricated a new macromolecular architecture of dual functional block copolymer brushes on the membranes by immobilization of initiator molecules to the sample surface with the aid of PDA, followed by grafting polymer brushes of poly (SBMA-b-MTAC) on membrane surfaces via activators regenerated by electron transfer-atom transfer radical polymerization (ARGET-ATRP). These membranes can effectively prevent the attachment of biofoulants and the formation of biofilms. In short, the surfaces can achieve excellent underwater oil-repellent property via whether grafting, deposition, coating, phase separation or copolymerization with zwitterionic polymers.^[36-38]

In this work, we report the surface modification of silk fabrics using zwitterionic poly (sulfobetaine methacrylate) (PSBMA) via enzymatic modification and surface-initiated atom transfer radical polymerization (SI-ATRP). Our results demonstrate that the PSBMA-modified silk fabrics show very large contact angle for oil-droplets in water, and have excellent oil resistance in air and in water-oil mixtures.

The PSBMA grafted silk fabrics were synthesized via a procedure of enzyme

pretreatment followed by an SI-ATRP reaction, as shown in Figure 1a and b. The papain enzyme was used to modify the silk fabrics. The enzymatic digestion step can remove sericin covered on the surface which endows the fabric higher surface area and exposure more surface amine (NH_2) groups. The NH_2 groups can react with the ATRP initiator α -bromoisobutyryl bromide (BIBB). This process is a robust and versatile method to prepare various polymer brushes on silk fabric surfaces via SI-ATRP. PSBMA polymer was grafted to the silk fabrics via an SI-ATRP reaction, lead to a superhydrophilic membrane, which showed excellent oil-resistance (Figure 1c) due to the hydration of the zwitterionic PSMBA.

Figure 1. Schematic illustration of the synthesis process used to construct PSBMA grafted fabrics with underwater superoleophobicity (a) and the preparation of zwitterionic polymer brush via ATRP (b). The mechanism diagram of oil resistance (c).

We used XPS and ATR-FTIR to characterize the silk fabric samples before and after the SI-ATRP modification. The XPS wide spectra of the silk fabrics are exhibited in Figure 2a, and the surface chemical compositions (atomic percent) of pristine, BiBB modified, and PSBMA grafted fabrics are shown in Table S1. Compared with the pristine sample, a new peak Br 3d (~ 69 eV) appeared in the spectrum of the BiBB modified fabric, indicating the successful incorporation of Br-containing functional groups. For the spectrum of the PSBMA grafted silk fabric, a new peak S 2p (~ 168 eV) was detected during the measurement, which was due to the sulfobetaine moiety the

grafted PSBMA. The high-resolution spectrum of S 2p (Figure 2b) shows the S 2p₁ (~ 168.1 eV) and S 2p₃ (~ 166.9 eV) peaks that can be attributed to the sulfonate groups in PSBMA.^[39] Furthermore, from the ATR-FTIR spectrum of PSBMA modified silk fabric, the new characteristic peak at 1041 cm⁻¹ were assigned to the asymmetric stretching of O=S=O from the grafted polymer (Figure 2c and S1). Both XPS and ATR-FTIR results confirmed the successful PSBMA modification on the silk fabric surface. TGA results of blank silk fabric and the PSBMA modified silk showed that the weights of both samples decreased from 250 to 350 °C. However, the PSBMA modified silk sample showed a more significant weight loss due to the decomposition of grafted polymer (Figure 2d).

Figure 2. (a) Wide XPS spectra (a) of pristine fabric membrane, BiBB grafted fabric membrane and PSBMA grafting fabric membrane. The high resolution S 2p (b) spectrum of PSBMA modified silk fabric. ATR-FTIR of the pristine silk fabric and PSBMA grafted silk fabric (c) and the TGA curves of pristine, papain-etching silk fabric and PSBMA grafted silk fabric, respectively (d).

We further used scanning electron microscopy (SEM) to characterize the surface morphology of the PSBMA modified silk fabrics. The SEM image of the pristine fabrics showed a smooth surface structure (Figure 3a), whereas a grooved structure appeared on the surface of enzymatically digested silk fabric (Figure S2) as the silk fibroin was partially dissolved by the papain enzyme. There was no significant change of the surface morphology after the PSBMA polymerization in comparison with the enzymatically digested silk fabrics (Figure 3b). However, energy dispersive spectroscopy (EDS) elementary analysis showed both S and N presented on the PSBMA modified silk membrane surface due to the SBMA moieties (Figure 3c), whereas only N was detected from the pristine silk sample (Figure S3). AFM measurements also revealed that the PSBMA modified fabric sample had a much rougher surface with an R_q of 58.5 nm. In comparison, the R_q of a pristine fabric surface was only 4.6 nm. (Figure 3e and f).

Figure 3. SEM images of pristine silk fabric (a) and PSBMA modified silk fabric (b).

The EDS mapping of PSBMA modified fabric (c and d). AFM images of the surface of pristine silk fabric (e) and PSBMA modified silk fabric (f), respectively. Corresponding (g) and (h) are the water contact angle images of pristine silk fabric and PSBMA modified silk fabric change with time.

Contact angle measurements (Figures 3g, h and Figure S5) showed that the BiBB grafting turned the hydrophilic pristine silk fabric surface to a hydrophobic surface, with a water contact angle of 126.8° . After the ATRP reaction, the PSBMA modified silk fabric surface became superhydrophilic again (Figure S5), indicating that the successful grafting of PSBMA on the fabric surface. Additionally, water can spread more rapidly on the PSBMA modified silk surface. It only took 0.3 second for the water droplet to spread on a PSBMA modified silk surface in comparison to 1.2s for the pristine silk fabric, which indicates that the PSBMA modified silk fabric is more hydrophilic than the pristine silk fabrics.

Figure 4. Schematic of oil contact angle underwater of pristine silk fabric (a) and schematic for the formation of zwitterionic@fabric for underwater super-anti -oil-adhesion (b). Inserts of a and b are the corresponding oil contact angles. The underwater

contact angle of different oil on the PSBMA modified silk fabric (c). The effect of pH of solution (d) and salt concentration (e) on oil contact angle under solution, respectively.

The hydrophilicity of pristine silk is mainly due to the hydrophilic residues of the silk proteins, such as amines and hydroxyl groups.^[40] Zwitterionic polymers are known to form strong hydration with the surrounding water molecules,^[41] and therefore lead to an increased hydrophilicity of the PSBMA modified silk fabrics. The superhydrophilicity of the PSBMA modified silk fabrics can lead to underwater superoleophobicity (Figure 4a and b). The underwater dichloromethane contact angles on the PSBMA polymer brush grafted fabrics resulted was 150.5° , while the control pristine silk fabric showed a contact angle of 114.2° (inserts of Figure 4a and b). The zwitterionic polymer layer grafted on the silk fabric surface can retain a strong hydration water layer between the oil droplet and the polymer layer, and thus effectively prevents the adhesion of oil and the surface, leading to a large underwater contact angle of the dichloromethane. As shown in Figure 4c, the PSBMA grafted fabrics exhibited underwater superoleophobicity to a variety of oils, such as hexane, kerosene, rapeseed oil, petroleum ether, toluene, and chloroform, all showing contact angles larger than 150° . Such underwater superoleophobic properties indicate that the PSBMA modified silk fabrics can be acted as effective anti-oil materials.

We further explored the effect of solution pH and salt concentration on anti-oil properties of the PSBMA modified silk fabrics. The dichloromethane contact angles on PSBMA modified silk fabrics showed no significant difference (150 - 151°) when changing the solution pH value from 1 to 11. This is expected as both the positive and negative charges of the sulfobetaine methacrylate modify are not strongly affected by the solution pH. However, the dichloromethane contact angle increased from $150.5^\circ \pm 0.8$ to $159.6^\circ \pm 0.7$ with increasing the NaCl concentration of solution from 0 to 1 mol/L (Figure 4e). The increased dichloromethane contact angle is likely due to the ‘anti-polyelectrolyte’ effect of zwitterionic polymers.^[42] Under salt-free solutions, the

zwitterionic sulfobetaine methacrylate monomers have inter- and intra-chain electrostatic interaction due to the oppositely charged groups and dipole-dipole interaction. Upon adding NaCl, the increase in the ionic strength decreases the Debye length and screens the electrostatic attractions between the zwitterionic sulfobetaine units and therefore expand the PSBMA chains. Such anti-polyelectrolyte effect has been observed in various zwitterionic polymers systems.^[43, 44] Consequently, the PSBMA brush layer can further swell, leading to a thicker hydrated polymer layer and larger oil contact angle in water.

The PSBMA chains grafted to the silk fabrics are strongly hydrated, which prevents the adsorption of oil onto the fabrics (Figure 5a). The PSBMA modified silk fabrics exhibit excellent underwater oil resistance. When dropping a droplet of 10 μ L dichlormethane with oil red O dye onto the surface of the PSBMA modified silk fabric (Figure 5b), the dichlormethane droplet stayed in a droplet form and did not spread on the fabric surface. This strongly indicate that the PSBMA modified silk fabrics can be used as anti-oil materials. To further evaluate the anti-oil performance of PSBMA modified silk fabric, we first dripped 20 μ L dichlormethane onto a dry pristine silk fabric and a PSBMA modified silk fabric. The dichlormethane can spread onto the dry fabric surfaces and turned the fabrics into red color due to the oil red O dye. Both samples were then stirred in water for 10 min. For the PSBMA grafted silk fabric sample, the dichlormethane was easily washed out after stirring and the fabric turned back to white color (Figure 5c), while the red contamination stayed on the pristine silk fabric surface (Figure 5d). These results suggested that the PSBMA grafted silk fabric have very good anti-oil properties.

Figure 5. Schematic of hydration of zwitterionic polymer in air for anti-oil (a). Optical image of the anti-oil performance of PSBMA grafted silk fabric underwater (b). Oil-cleaning performance of different samples: groups (c) and (d) are samples of untreated fabric and PSBMA grafted fabric.

Anti-oil materials are very important for a variety of applications. As far as we know, there are very few studies on the anti-oil properties of zwitterionic polymer grafted fabric materials. Our results demonstrated that the grafting of PSBMA enhanced the water wettability of the silk fabrics and the oil contaminants on the PSBMA modified silk fabrics can be easily washed away when immersed in water. With superhydrophilic and underwater superoleophobic properties, the PSBMA-grafted silk fabrics can be very useful in various anti-oil applications, such as oil-resistant clothing, anti-oil fouling, and water-oil separation.^[4, 45, 46] The straightforward modification

process of using papain enzyme and SI-ATRP can also be extended to fabricate surface modified silk fabrics with various surface functional polymers.

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Conflict of Interest

The authors declare no conflict of interest.

References

- [1] W. Zhang, N. Liu, Y. Cao, X. Lin, Y. Liu, L. Feng, *Adv. Mater. Interfaces* **2017**, *4*, 1600029.
- [2] J. Zhang, F. Zhang, A. Wang, Y. Lu, J. Li, Y. Zhu, J. Jin, *Langmuir* **2019**, *35*, 1682.
- [3] Z. Li, Z. Guo, *Nanoscale* **2019**, *11*, 22636.
- [4] Z.-M. Zhang, Z.-Q. Gan, R.-Y. Bao, K. Ke, Z.-Y. Liu, M.-B. Yang, W. Yang, *J. Membrane Sci.* **2020**, *593*, 117420.
- [5] S. Bai, X. Li, R. Zhang, C. Li, K. Zhu, P. Sun, Y. Zhao, L. Ren, X. Yuan, *Chem. Eng. J.* **2019**, *357*, 667.
- [6] Z. Chu, Y. Feng, S. Seeger, *Angew. Chem. Int. Ed.* **2015**, *54*, 2328.
- [7] S. Gao, J. Sun, P. Liu, F. Zhang, W. Zhang, S. Yuan, J. Li, J. Jin, *Adv. Mater.* **2016**, *28*, 5307.
- [8] J. Li, L. Yan, H. Li, W. Li, F. Zha, Z. Lei, *J. Mater. Chem. A* **2015**, *3*, 14696.
- [9] H. C. Yang, J. K. Pi, K. J. Liao, H. Huang, Q. Y. Wu, X. J. Huang, Z. K. Xu, *ACS Appl. Mater. Inter.* **2014**, *6*, 12566.
- [10] Z. Pan, S. Cao, J. Li, Z. Du, F. Cheng, *J. Membrane Sci.* **2019**, *572*, 596.
- [11] F. Zhang, W. B. Zhang, Z. Shi, D. Wang, J. Jin, L. Jiang, *Adv. Mater.* **2013**, *25*, 4192.
- [12] L. Xiong, W. Guo, B. M. Alameda, R. K. Sloan, W. D. Walker, D. L. Patton, *ACS Omega* **2018**, *3*, 10278.
- [13] Z. Xue, S. Wang, L. Lin, L. Chen, M. Liu, L. Feng, L. Jiang, *Adv. Mater.* **2011**, *23*, 4270.
- [14] W. Zhang, Y. Zhu, X. Liu, D. Wang, J. Li, L. Jiang, J. Jin, *Angew. Chem. Int. Ed.* **2014**, *53*, 856.
- [15] N. Shahkaramipour, T. N. Tran, S. Ramanan, H. Lin, *Membranes (Basel)* **2017**, *7*.
- [16] L. Yao, C. He, S. Chen, W. Zhao, Y. Xie, S. Sun, S. Nie, C. Zhao, *Langmuir* **2019**, *35*, 1430.
- [17] H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith, *Science* **2007**, *318*, 426.
- [18] J. Zhao, D. Li, H. Han, J. Lin, J. Yang, Q. Wang, X. Feng, N. Yang, Y. Zhao, L. Chen, *Langmuir* **2019**, *35*, 2630.

- [19] K. Hou, Y. Zeng, C. Zhou, J. Chen, X. Wen, S. Xu, J. Cheng, Y. Lin, P. Pi, *Appl. Surf. Sci.* **2017**, *416*, 344.
- [20] Y. Zhu, W. Xie, F. Zhang, T. Xing, J. Jin, *ACS Appl. Mater. Inter.* **2017**, *9*, 9603.
- [21] P. Bengani-Lutz, E. Converse, P. Cebe, A. Asatekin, *ACS Appl. Mater. Inter.* **2017**, *9*, 20859.
- [22] C. J. Huang, Y. Li, S. Jiang, *Anal. Chem.* **2012**, *84*, 3440.
- [23] P. Kaner, E. Rubakh, D. H. Kim, A. Asatekin, *J. Membrane Sci.* **2017**, *533*, 141.
- [24] Y. Higaki, J. Nishida, A. Takenaka, R. Yoshimatsu, M. Kobayashi, A. Takahara, *Polym. J.* **2015**, *47*, 811.
- [25] M. Kobayashi, Y. Terayama, H. Yamaguchi, M. Terada, D. Murakami, K. Ishihara, A. Takahara, *Langmuir* **2012**, *28*, 7212.
- [26] P. H. H. Duong, K. Daumann, P. Y. Hong, M. Ulbricht, S. P. Nunes, *Langmuir* **2019**, *35*, 1284.
- [27] C. Shi, B. Yan, L. Xie, L. Zhang, J. Wang, A. Takahara, H. Zeng, *Angew. Chem. Int. Ed.* **2016**, *55*, 15017.
- [28] C. F. Santa Chalarca, R. A. Letteri, A. Perazzo, H. A. Stone, T. Emrick, *Adv. Funct. Mater.* **2018**, *28*, 1804325.
- [29] L. Ni, J. Meng, G. M. Geise, Y. Zhang, J. Zhou, *J. Membrane Sci.* **2015**, *491*, 73.
- [30] S. Shah, J. Liu, S. Ng, S. Luo, R. Guo, C. Cheng, H. Lin, *J. Polym. Sci. Part B Polym. Phys.* **2016**, *54*, 1924.
- [31] C. C. Chang, K. W. Kolewe, Y. Li, I. Kosif, B. D. Freeman, K. R. Carter, J. D. Schiffman, T. Emrick, *Adv. Mater. Interfaces* **2016**, *3*.
- [32] T. Yuan, J. Meng, T. Hao, Z. Wang, Y. Zhang, *ACS Appl. Mater. Inter.* **2015**, *7*, 14896.
- [33] C. Wang, Z. Li, J. Chen, Y. Zhong, Y. Yin, L. Cao, H. Wu, *J. Membrane Sci.* **2018**, *548*, 194.
- [34] Y. Zhu, J. Wang, F. Zhang, S. Gao, A. Wang, W. Fang, J. Jin, *Adv. Funct. Mater.* **2018**, *28*, 1804121.
- [35] G. Ye, J. Lee, F. Perreault, M. Elimelech, *ACS Appl. Mater. Inter.* **2015**, *7*, 23069.
- [36] Y. Deng, G. Zhang, R. Bai, S. Shen, X. Zhou, I. Wyman, *J. Membrane Sci.* **2019**, *569*, 60.
- [37] P. Li, Q. Ge, *ACS Appl. Mater. Inter.* **2019**, *11*, 31328.
- [38] Y. Sun, Y. Zong, N. Yang, N. Zhang, B. Jiang, L. Zhang, X. Xiao, *Sep. Purif. Technol.* **2020**, *234*, 116015.
- [39] A. Lamberti, M. Serrapede, G. Ferraro, M. Fontana, F. Perrucci, S. Bianco, A. Chiolerio, S. Bocchini, *2D Mater.* **2017**, *4*, 035012.
- [40] G. Freddi, R. Mossotti, R. Innocenti, *J. Biotechnol.* **2003**, *106*, 101.
- [41] X. Zhang, J. Tian, S. Gao, W. Shi, Z. Zhang, F. Cui, S. Zhang, S. Guo, X. Yang, H. Xie, D. Liu, *J. Membrane Sci.* **2017**, *544*, 368.
- [42] S. Xiao, Y. Zhang, M. Shen, F. Chen, P. Fan, M. Zhong, B. Ren, J. Yang, J. Zheng, *Langmuir* **2017**, *34*, 97.
- [43] F. Wang, J. Yang, J. Zhao, *Polym. Int.* **2015**, *64*, 999.
- [44] M. Gao, K. Gawel, B. T. Stokke, *Eur. Polym. J.* **2014**, *53*, 65.
- [45] B. Su, Y. Tian, L. Jiang, *J. Am. Chem. Soc.* **2016**, *138*, 1727.
- [46] S. Li, P. Huang, Z. Ye, Y. Wang, W. Wang, D. Kong, J. Zhang, L. Deng, A. Dong, *J. Mater. Chem. B* **2019**, *7*, 6024.

TOC

We developed a highly anti-oil fabric membrane by surface grafting of zwitterionic poly (sulfobetaine methacrylate) (PSBMA) onto enzymatically modified fabric surface via surface-initiated atom-transfer radical polymerization (SI-ATRP). The PSBMA modified fabric membrane exhibited increased surface roughness and improved superhydrophilicity. The fabrics also showed excellent oil resistance in air and in water-oil mixtures.