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1   **Investigation of one-dimensional multi-functional zwitterionic Ag**

2   **nanowire as a novel modifier for PVDF ultrafiltration membrane**

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8

9   **Abstract**

10   This work presented a novel kind of one-dimensional multi-functional modifier for

11   membrane materials. Cysteine modified silver nanowires (C-AgNW) were used to modify

12   polyvinylidene fluoride (PVDF) membranes and the comprehensive optimized properties

13   including separation efficiency, mechanical strength and antifouling ability of PVDF

14   membranes demonstrated that monodisperse, orientated and zwitterionic C-AgNW was an

15   efficient modifier for PVDF ultrafiltration membrane. The objective of this work was to

16   comprehensively improve the application performance of polymer materials by the special

17   hybrid mechanism of one-dimensional nanomaterials.

18   **Keywords**: polyvinylidene fluoride, one dimension, zwitterion, silver nanowires

19   **1. Introduction**

20   In recent years, membrane technology as indispensable separation process has been into

21   the rapid development period and widely used in the fields of water treatment, industrial,

22   pharmaceutical, seawater desalination, food and energy due to the outstanding features of

23   high efficiency, energy saving and easy to control.[1] The ultrafiltration (UF) and

1   microfiltration (MF) technologies with hydrophobic polyvinylidene fluoride (PVDF),

2   polypropylene(PP), polyether sulfone(PES), polyvinyl chloride (PVC) as membrane materials

3   have been extensively commercialized base on the mature control and application

4   mechanism,[2-5] and enhancing the application performance of these polymer membranes by

5   efficient modification is the focus research of membrane technology at this stage. For

6   example, UF technology shows an increasingly important role in the field of water security,

7   and many families have installed UF membrane module to insure the quality of domestic

8   water, so the preparation of efficient, antifouling and antibacterial UF membrane has become

9   an urgent demand of UF membrane industry.

10   High separation efficiency, high membrane strength, excellent antifouling performance are

11   three main requirements for the applied UF membranes.[6] The commercial UF membrane at

12   present stage can exhibit appropriate separation efficiency and strength, but the fouling

13   resistance is poor. In addition, many literatures have reported the modification research of UF

14   membrane materials, but only one or two parameters of separation efficiency, strength and

15   fouling resistance for UF membranes can be improved at the same time by the variety of

16   modification methods.[7-10] For instance, blending amphiphilic copolymer is capable of

17   achieving fouling resistance with decreased strength, while the surface grafting method with

18   improved antifouling property and clogged membrane pores is stuck in the experimental

19   stage due to the complex reaction conditions.[11-12]

20   Several conditions must be met as the effective modifier for UF membrane, the modifier

21   should be functional, the executed modified method should be simple and easy, and modifier

22   should interact with the matrix material to exhibit positive effect.[13-15] Efficient

1   organic-inorganic hybrid way is conducive to take full advantage of two types of materials,

2   and using functional nanomaterials such as hydrophilic nanoparticles, modified graphene and

3   carbon nanotubes to hybrid polymer membrane material is a common method for the

4   optimization of membrane properties.[16-18] But the biggest problem limiting the application of

5   nanomaterials is the dispersion problem, agglomerated nanoparticles always exist after hybrid,

6   restricting the efficiently function of nanomaterials. In recent years, more and more attention

7   has been paid to the one-dimensional materials,[19,20] which not only possess the characteristics

8   of nanomaterials such as large surface area, high strength and high activity, but also exhibit

9   special advantages of high dispersion and high orientation due to the length-diameter (L/D)

10   ratio. Our previous studies[21] found that blending linear chitin nanocrystals was conducive to

11   enhance the overall performance of PVDF membrane, and one-dimensional functional

12   nanomaterials are potential modifier for hybridization.

13   In addition, zwitterionic materials[22-24] can exhibit the great promising antifouling capacity

14   for antifouling modification of membrane materials. All the betaine based and amino acids

15   based zwitterionic materials exhibit superior ability to inhibit nonspecific adsorption of

16   pollutants, every ion pair of positive and negative groups can bind vast of water molecules

17   around and form a protective water layer on materials surface, which shields the hydrophobic

18   interactions between the pollutants and membrane surface. As far as we know, Cysteine as a

19   new kind of zwitterionic antifouling coating material is particularly desirable due to sample

20   and convenient reaction of thiol chemistry.[25]

21   In this paper, cysteine modified silver nanowires (C-AgNW) were prepared though simple

22   synthetic method, which was an extraordinary one-dimensional nanomaterial with

1 multifunction such as fouling resistance of zwitterion, antibacterial activity of Ag and high

2 dispersion of nanowire. A trace amount of C-AgNW was used to hybrid PVDF membrane,

3 and the separation performance, membrane strength, antifouling properties and antibacterial

4 properties of modified PVDF membrane were investigated, this paper aims to provide a new

5 idea for hybrid modification.

6 **2. Experiments**

7 **2.1 Materials**

8 Polyvinylidene fluoride (PVDF, MG15) was purchased from Arkema. Polyethylene glycol

9 (PEG, Mw~20000), polyvinylpyrrolidone (PVP, K30, Mw~40000), silver nitrate (AgNO3)

10 and bovine serum albumin (BSA, Mw~67000) were purchased from Sinopharm Chemical Co.

11 (China). Humic acid (HA, fulvic acid＞90%）was purchased from Aladdin. Ethylene glycol

12 (EG), N, N-dimethylacetamide (DMAC) and ethanol were of analytical grade, all aqueous

13 solutions were prepared with deionized water. All the reagents were used as received without

14 further purification.

15 **2.2 Preparation of C-AgNW**

16 Ag nanowires were prepared according to the reported method[26] using the three step

17 reaction way. The first generation of AgNW was prepared as followed modified

18 CuCl$_2$-mediated polyol process. Cu-additive solution (40 μL of a 4 mM CuCl$_2$ solution in

19 EG), 1.5 ml of 140 mM PVP solution and 1.5 ml of 95 mM AgNO$_3$ solution were added

20 sequentially to 5 ml of ethylene glycol (EG) at 151.5℃ to prepare 1st generation of AgNW,

21 which were condensed for the next growth step. The growth reaction steps were executed

22 continuously, and the length of the AgNW increased with increasing number of reaction. 5 ml

1   of EG, Cu-additive and 5ml PVP solution were mixed and heated for 1 h at 151.5 ℃ under

2   stirring, followed 1 ml 1st generation AgNW solution is injected into above solution, and 1.5

3   ml of the same $AgNO_3$ solution was injected slowly. After the reaction, Ag nanowires were

4   collected by centrifugation for the followed use. The cleaned AgNW with alcohol-water

5   mixture was added into cysteine solution (10g/L, PBS, pH7.4) under magnetic stirring at

6   room temperature to react for 1 hour. Finally, the product was collected by filtration with

7   PTFE microporous membrane (0.22um).

8   **2.3 Preparation of hybrid PVDF membrane**

9   The hybrid PVDF membranes were prepared through non-solvent induced phase

10   separation (NIPS) method, a certain amount of AgNW was added into the casting solution of

11   PVDF/PEG/DMAC (10g/5g/50g), and these homogeneous solution were casted on the glass

12   following the same direction and intensity with steel knife every time. The added mass ratios

13   of AgNW to PVDF were 0.5%, 1%, 1.5% and 3% and these prepared hybrid PVDF

14   membranes were labeled C-AgNW-0.5%, C-AgNW-1%, C-AgNW-1.5% and C-AgNW-3%,

15   respectively.

16   **2.4 Membrane characterization**

17   Mechanical strength of modified PVDF membrane was tested using a tensile testing

18   machine with the stretching speed of 20mm/min. The differential scanning calorimeter (DSC,

19   TA-Q20, America) was employed to investigate the crystallization enthalpy of modified

20   PVDF membranes with ramp rate of 10℃/min. Surface morphologies of membranes were

21   viewed with the field emission scanning electron microscope (SEM, Hitachi SU8010, Japan),

22   cross-section morphology of membranes were observed by environmental scanning electron

1 microscope (ESEM, Quanta-250, FEI). X-ray photoelectron spectroscopy (XPS, Kratos,

2 AXIS UltraDLD) was used to analysis the elemental composition of the modified nanowire.

3 The water contact angles (CA) on the membranes were measured by OCA40Micro

4 (Dataphysics Co., Germany) at $25°C$ to evaluate the surface wetting ability with the drop

5 shape image analysis system.

6 **2.5 Separation experiments**

7 The separation performances of neat and modified PVDF membranes were investigated

8 using a dead-end filtration system with affective membrane area of 12 cm^2. All the filtration

9 experiments were carried out with the operation pressure at 0.1 MPa, and stable water flux

10 J_1(L/m^2h)was obtained using pure water as feed and calculated as equation (1). The rejection

11 was tested with BSA solution (1g/L, pH7.4) as feed solution, the BSA concentrations of feed

12 and permeate were examined via UV spectrophotometer (UV-1800, Shimadzu) with

13 characteristic wavelength at 280 nm and calculated as equation (2).

14 $$J_1 = V/A \times t \tag{1}$$

15 $$R = (1 - C_P/C) \times 100\% \tag{2}$$

16 Where V (L) is the volume of permeated water, t (h) is the permeation time and A (m^2) is

17 effective area for filtration. Cp and C are contributed to the BSA concentration of permeate

18 and feed solution.

19 **2.6 Fouling experiments**

20 The dynamic fouling experiments were executed using alternate feed solution of pure

21 water and pollutants solution. BSA solution (1g/L, pH 7.4) and HA (1g/L) were used as

22 pollutants feed, respectively. Firstly, stable water flux was recorded as J_1, then the feed was

1   replaced with pollutants solution and stable flux was recorded as J_p, after that, the tested

2   membranes were washed with pure water for 20 minutes and the secondary pure water flux

3   was obtained as J_2.Water flux recover ratio (FRR) value and irreversible fouling ratio (IFR)

4   value were calculated by the followed equation (3) (4), respectively.

5    $$FRR = J_2/J_1 \times 100\% \qquad\qquad (3)$$

6    $$IFR = 1 - FRR \qquad\qquad (4)$$

7   **2.7 Antimicrobial assessment**

8   The antibacterial activities of the modified PVDF membranes were investigated using the

9   Gram positive bacteria S. aureus and Gram negative E. coli according to the reported

10   method[27]. All containers and membranes were previously sterilized. Bacterial colonies were

11   cultivated in 20 ml of a 3.1% yeast-dextrose broth (containing 8 g/L beef extract, 10 g/L

12   peptone, 5 g/L glucose, 5 g/L sodium chloride, and 3 g/L yeast extract at pH of 6.8) at 37℃.

13   0.1 ml of the bacteria suspension was pipetted out and added into 50 ml of 3.1%yeast–

14   dextrose broth and resuspended bacterial solution was at the concentration of 10^6 cells/ml.

15   About 100 mg of modified PVDF membranes were immersed into the 50 ml bacterial

16   suspension and the suspension was shaken at 37 for 2 h, 0.1 ml of the bacteria suspension

17   was pipetted out from the flask and added 0.9 ml PBS. Then 0.1 ml of the diluted suspension

18   was spread onto a triplicate solid agar plate, which was sealed and incubated at 37℃ for 24 h.

19   Finally, the numbers of the viable cells were counted. Each antibacterial efficacy in repeated

20   detections was investigated for three times and a control experiment was carried out using

21   100 mg of neat PVDF membrane.

22

1 ### 3. Results and discussion

2

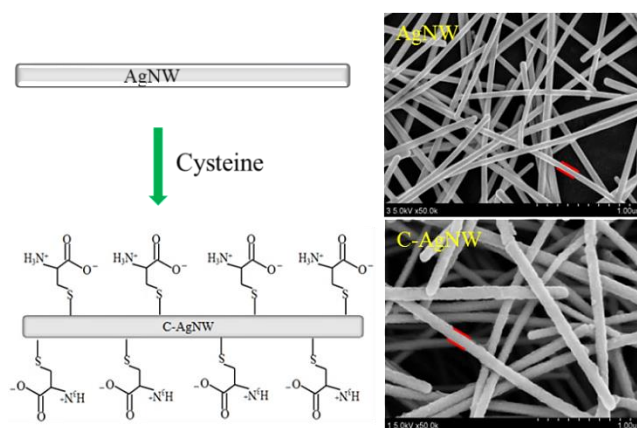4   Fig.1. Zwitterionic modification of AgNW and the corresponding SEM images.

5   Table 1. XPS quantified elemental atomic percentages of C-AgNW.

Sample/Element	Atomic concentration (%)				
	Ag	C	S	N	O
AgNW	99.55	0.12	0	0	0.33
C-AgNW	91.05	3.91	1.27	1.29	2.48

6

7   Nanowires, one-dimensional functional nanomaterial, could be used as a new type of

8   nanoscale additives,[20] hybrid method was conducive to demonstrate the functionality of

9   one-dimensional nanomaterials by investigating the changed performance of matrix materials.

10   Because cysteine contained a thiol group and a pair of ionogenic amino and carboxyl, which

11   were thought as a natural source of zwitterion, and it was known that cysteine could fabricate

12   antifouling coating with several nanometers thickness on gold surface.[25] As shown in Fig. 1,

13   AgNW was prepared by the reported method,[26] schematic described cysteine was used as a

14   coating material and anchored onto the AgNW surface through thiol chemistry. According to

1   the SEM results, the prepared silver nanowires showed a large L/D ratio, smooth surface and

2   uniform diameters (about 85nm) without significant aggregation. After surface modification

3   with cysteine, the C-AgNW exhibited increased diameter and rough surface, indicating

4   cysteine coating was fixed onto the surface of AgNW through quick and easy thiol chemistry

5   reaction. The detected N and S elements (Table 1) in modified nanowires were attributable to

6   the feature element composition of cysteine. The literature[25] reported when the cysteine was

7   anchored onto material surface in PBS buffer, the majority (about 90%) of amino and

8   carboxy groups were ionic state (NH_3^+ and COO^-), so it could be inferred that C-AgNW was

9   a one-dimensional material with cysteine-type zwitterionic surface.

10   Because C-AgNW was a kind of one-dimensional nanomaterials, the unique feature of

11   high length-diameter ratio not only improved the dispersion by reducing the conventional

12   agglomeration prone of nanomaterials, but also increased the chances of being oriented. In

13   the preparation of flat membranes and hollow membranes, fixed orientation force of casting

14   or drawing was always additionally used to promote the shaping of membrane material,

15   One-dimensional C-AgNW and PVDF chains were simultaneously oriented in the orientation

16   process as shown in Fig. 2A. According to the surface and cross section SEM images of

17   C-AgNW-1% membrane, it was clearly seen all the added C-AgNW were arranged in the

18   same direction. Especially the surface SEM image, all seen C-AgNW were strictly

19   arrangement in accordance with the same direction, exhibited excellent orientation effect, and

20   all the C-AgNW were single, showing explicit monodispersity. Tensile strength and breaking

21   elongation of PVDF membranes before and after hybrid modification were shown in Fig.2B,

22   it was clearly seen that a significant increase in strength of the PVDF membrane after

1   blending C-AgNW was observe. Compared with the tensile strength value of neat PVDF

2   membrane, the tensile strength of C-AgNW-3% membrane was elevated to 190%, and there

3   were no significant decline for the breaking elongation. Fig. 2C showed the significant

4   increase of the crystallization peak intensity of the hybrid PVDF membrane, crystallization

5   enthalpy of C-AgNW-1.5% membrane increased from 30.85J/g (PVDF membrane) to

6   43.98J/g, the elevated proportion was more than 40%, which was directly contribute to the

7   increase of membrane strength. Meanwhile, according to Fig. 2A, the C-AgNW directly

8   embedded in the PVDF matrix without visible defects on the membrane surface and

9   contacted with the PVDF molecular chain. Based on these results, it could be inferred that the

10   increased membrane strength was related with the changed crystallinity of PVDF membrane,

11   and these two parameters were positively correlated. The increased degree of crystallinity of

12   modified PVDF membrane should be resulted from the orientated one-dimensional C-AgNW

13   in PVDF matrix. C-AgNW, as inorganic-organic hybrid material with hard texture and high

14   L/D ratio, showed a tendency to be easily oriented, and provided the impetus for the

15   orientation of the surrounding polymeric segments during orientated process. Each

16   orientation of C-AgNW would drive the PVDF segments around to be oriented and a large

17   number of PVDF segments with ordered arrangement also resulted in the increase of

18   crystallinity degree of the modified PVDF membranes, which exhibited increased tensile

19   strength at the macro level. So adding one-dimensional C-AgNW material was beneficial to

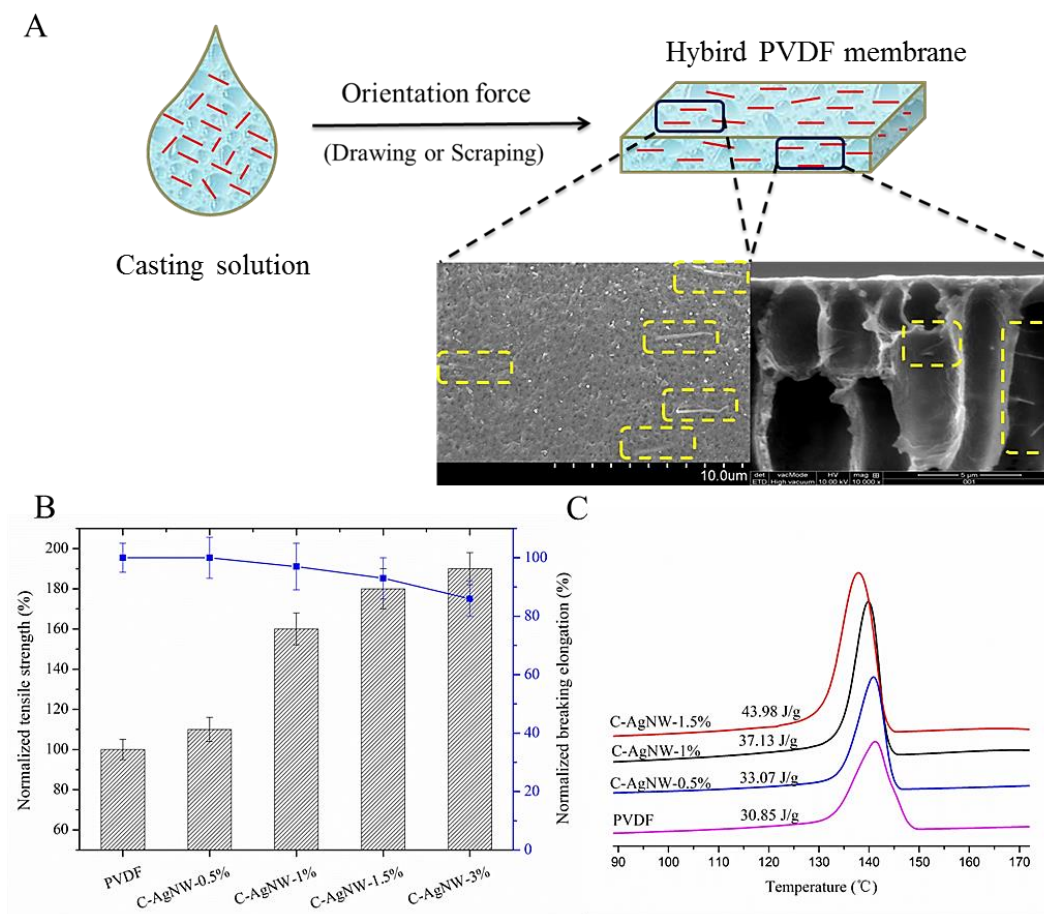20   increase the mechanical strength of PVDF membrane.

Fig. 2. A: the orientation diagram of C-AgNW in PVDF membrane and the corresponding
SEM images of C-AgNW-1%, B: normalized tensile strength and breaking elongation of neat
and modified PVDF membranes, C: DSC curves and crystallization enthalpy of neat and
modified PVDF membranes.

After hybrid of PVDF membranes with trace amount of C-AgNW, the separation

efficiency of water flux and rejection of hybrid PVDF membranes were investigated,

commonly used BSA was selected as the interception media. Because silver was a precious

metal, the amount of hybrid AgNW was no more than 3% due to the perspective of economic

benefits. As seen from Fig. 3A and Fig. 3B, more pores were observed on the C-AgNW-1.5%

membrane surface than neat PVDF membrane. As shown in Fig. 3C, the modified PVDF

membranes exhibited the improved wetting ability with the CA of C-AgNW-1.5% membrane

1   and C-AgNW-3% decreasing to 71 ° and 66 °, respectively. Fig. 3D showed the water flux and

2   rejection rate of PVDF membrane was 94 L/m^{2}h and 75%, nevertheless, the water flux and

3   rejection rate of C-AgNW-3% membrane increased to 159 L/m^{2}h and 93%, respectively,

4   Furthermore, the simultaneously increased flux and rejection breaks the conventional

5   trade-off phenomenon, indicating the added one-dimensional C-AgNW was conducive to

6   improve the separation efficiency of PVDF membrane. The improved separation performance

7   of modified PVDF membrane should be attribute the enhanced wetting ability on membrane

8   surface and matrix to C-AgNW. The blended hydrophilic C-AgNW in casting solution was

9   conducive to increase the probability of forming membrane pores by delaying the rapid

10   exchange of water and solvent DMAC, which contributed to the flux increase. As

11   zwitterionic nanowires, there were a lot of ionogenic amino and carboxyl groups on the

12   surface of C-AgNW, these active amino and carboxyl groups could show strong

13   hydrophilicity though ionic hydration and hydrogen bonding in the aquatic environment,

14   therefore, a large number of water molecules could be gathered around the C-AgNW to

15   generate a particular wetting environment. After hybrid, every C-AgNW uniformly

16   distributed in membrane surface and matrix was able to form a slender hydrophilic region in

17   water due to the L/D ratio, the improved microscopic wetting properties of PVDF membrane

18   surface and matrix were conducive to the adsorption and permeate of water molecules, and

19   enhance the exclusion and screening ability for hydrophobic BSA molecules to obtain the

20   optimized rejection. The more C-AgNW amount added, the greater the enhanced proportion
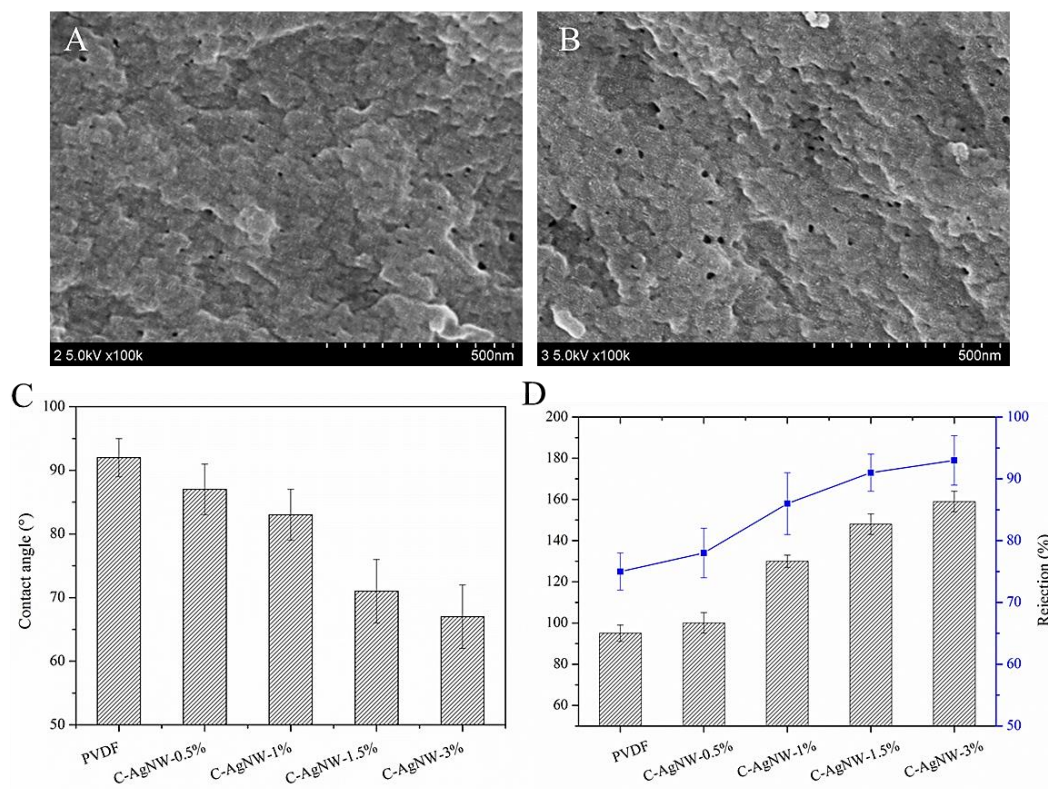
21   of flux and rejection.

Fig. 3. A: surface morphology of PVDF membrane, B: surface morphology of

C-AgNW-1.5% membrane, C: water contact angles, D: separation performances.

As one kind of hydrophobic material, PVDF membrane was prone to induce serious

membrane fouling problem during dynamic separation process, which would reduce the

separation efficiency and shorten the service life of membrane module. The secondary water

flux recovery ratio (FRR) values were used to quantify the antifouling ability of modified

PVDF membranes. The high FRR values (low IFR values) indicated the better antifouling

performance of PVDF membranes and less irreversible pollutants remained in the PVDF

membranes. As shown in Fig. 4, after the filtration of BSA pollutant solution, the FRR value

of PVDF membrane was only 55%, the FRR value of C-AgNW-3% membrane increased to

87%. For the pollutant HA, FRR values of PVDF membrane, C-AgNW-1%, C-AgNW-1.5%

1 and C-AgNW-3% membranes were 65%, 83%, 91% and 93%, respectively. It was clear that

2 the antifouling performance of PVDF membranes were significantly increased after adding

3 C-AgNW. The reason should be attributed to the zwitterionic antifouling characteristics of

4 C-AgNW. After C-AgNW being evenly distributed in the PVDF membrane, zwitterionic

5 surface of C-AgNW was capable of changing the surrounding microenvironment of PVDF

6 surface and matrix due to the super hydrophilicity, wetting properties and antifouling

7 performance of zwitterionic groups, the microenvironment of modified PVDF membrane

8 could be improved with zwitterionic C-AgNW and the manifested fouling-resistance

9 properties were conducive to reduce the possibility of adsorption and accumulation of

10 pollutants in PVDF matrix, whereby original irreversible pollutants were converted to

11 reversible pollutants, which could be washed away by flushing to obtain the high FRR values.
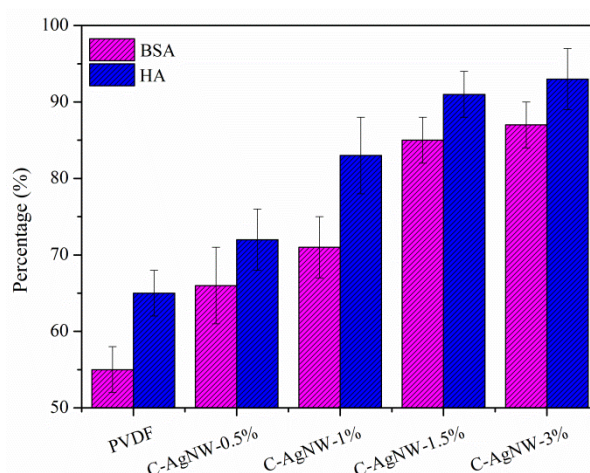
12

13 Fig. 4. Antifouling performances of neat and modified PVDF membranes with BSA and

14 HA as pollutants feed.

15 In addition, the antimicrobial properties of the modified PVDF membranes were

16 investigated. Nowadays, silver was considered to be the best antibacterial material, the

17 bactericidal rates of Ag for various kinds of bacteria were more than 99%, nano-silver was

1   also a potent antimicrobial agent, could exhibit excellent antibacterial properties in many

2   areas, and AgNW was able to retain the unique characteristics of sterilization. The

3   antimicrobial experiments of Escherichia coli and Staphylococcus aureus of modified PVDF

4   membranes were tested though reported method[27] and the results are shown in Table 2,

5   according to the three parallel testing, the bacteria mortalities of C-AgNW-1.5% membrane

6   were no less than 98%. Modified membrane exhibited significant antibacterial activity for

7   these common Gram bacteria due to the one-dimensional C-AgNW.

8

9   Table 2. Bacteria mortality of hybrid PVDF membranes.

	Bacteria mortality of three samples (%)		
	PVDF	C-AgNW-0.5%	C-AgNW-1.5%
E. coli	0 %	97%	99%
S. aureus	0 %	98%	99%

10

11   **4. Conclusions**

12   One-dimensional and multi-functional C-AgNW was used to prepare novel PVDF UF

13   membrane. A spot of C-AgNW was conducive to optimize all the performance of PVDF

14   membrane, the performance test results of hybrid C-AgNW-3% membrane showed that the

15   water flux increased about 70% along with improved BSA rejection, the tensile strength was

16   upgraded by 90%, and the FRR values were no less than 85% for BSA and HA pollutants and

17   excellent antibacterial activity of hybrid PVDF membrane were also observed for S. aureus

18   and E. coli. Although a single performance parameter of modified PVDF membrane was not

1 as good as the commercial membrane or the reported modified PVDF membranes, the

2 enhanced ratios of comprehensive performance parameters of modified PVDF membranes

3 demonstrated C-AgNW was an effective modifier for PVDF membrane to enhance the

4 overall application performance, also provided a new idea of using trace one-dimensional

5 materials to modify polymer materials.

6

Acknowledgement

12

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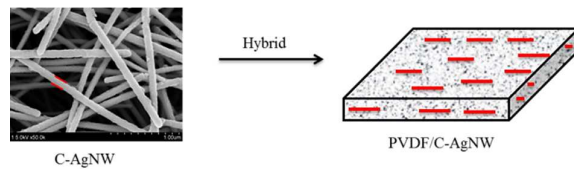
The blended zwitterionic Ag nanowires improve the mechanical strength, separation property and fouling resistance of PVDF ultrafiltration membrane.