Supporting Information

Performance of Novel Ag-n-TiO_2/PVC Reinforced Hollow Fiber Membrane Applied in Water Purification: *In-Situ* Antibacterial Property and Resistance to Biofouling

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Summary:

13 pages, including 8 Figures and 3 Tables

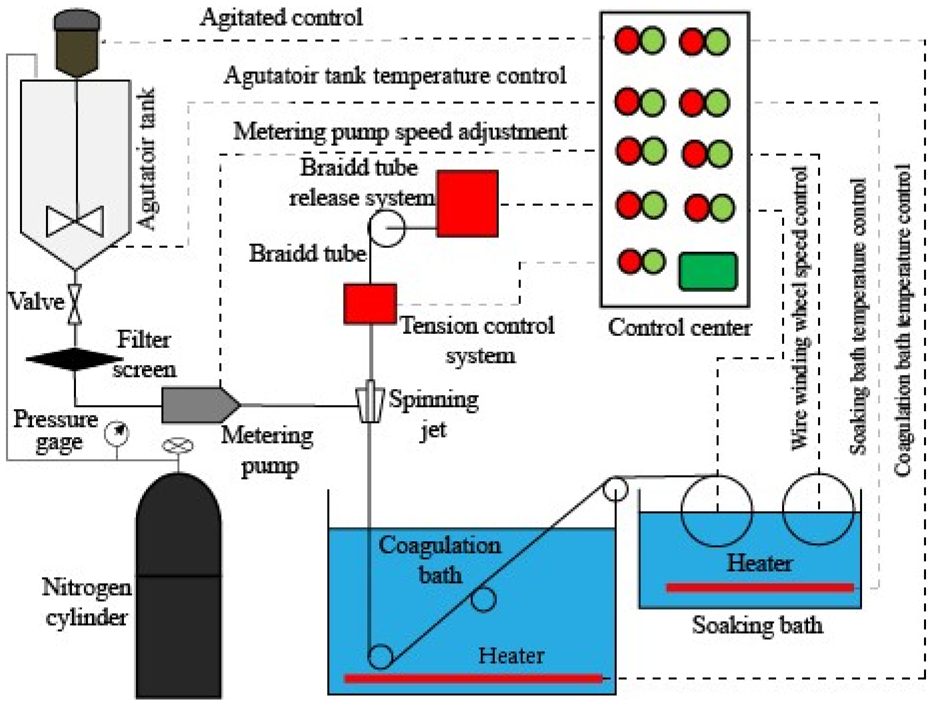

Fig. S1 Schematic diagram of reinforced hollow fiber membrane preparation machine

The Schematic diagram of reinforced hollow fiber membrane preparation machine is shown as Fig.S1. The agutatoir tank was used to stir, degas, and store the dope solution, and its agitated temperature and speed can be adjusted by the control center. Metering pump was utilized to control the flow of the dope solution. Both braidd tube release system and tension control system were used to control the tension of the braidd tube. Generally, when we controlled the tension of the braidd tube as small as possible, the cross-section of the prepared reinforced hollow fiber membrane tended to be cylindrical.

The agitator tank was connected with a N_2 gas cylinder. Basically, the dope was dispensed under pressure through a spinning jet at a controlled rate, and passed through an air gap before immersing into a coagulation bath. After the nascent hollow fibers entered the soaking bath, the fibers were taken up by a wire winding wheel and stored in a water bath to remove residual solvent for at least 2 days. Since the membrane pores should be kept in long time, the prepared membranes were further rinsed into the mixtures of tap water and glycerinum (V/V=1:1) for 24 h. The hollow fiber membranes were dried in air at ambient temperature and then divided into bundles for further post-treatments. Prior to the spinning process, all the pipelines were filled with dope solution without any air bubbles and the braidd tube was adjusted to the center of spinning jet.

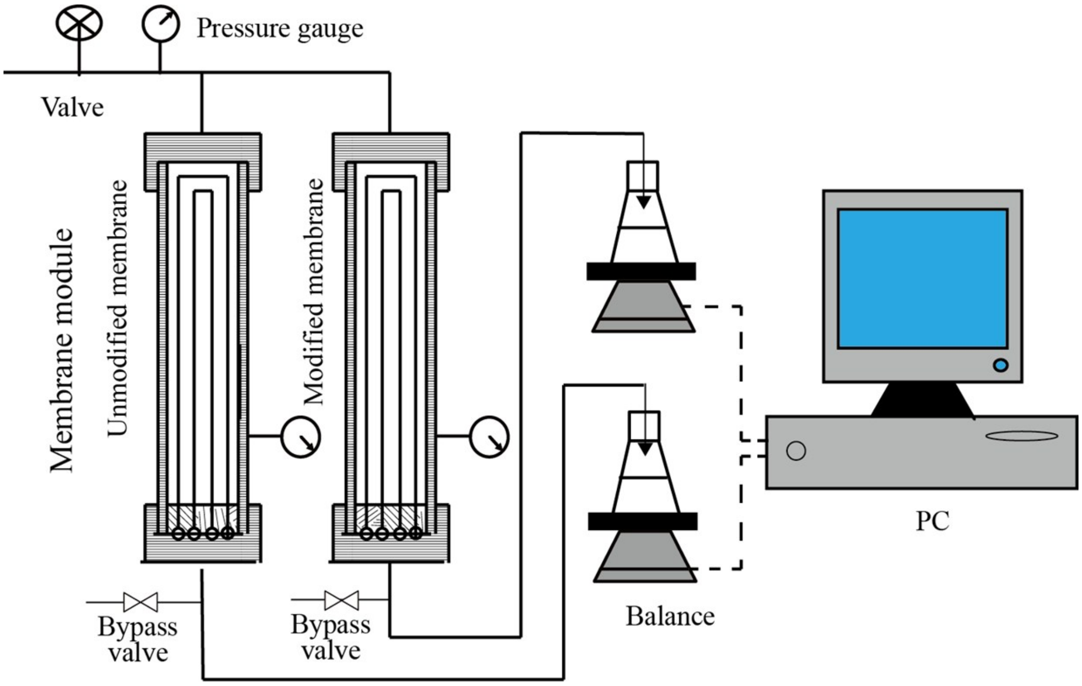

Fig. S2 Experimental schematic of the UF experimental setup for long term biofouling analysis: the influent pressure was 0.1 MPa, the effective membrane area of every membrane module was 0.1695 m^2

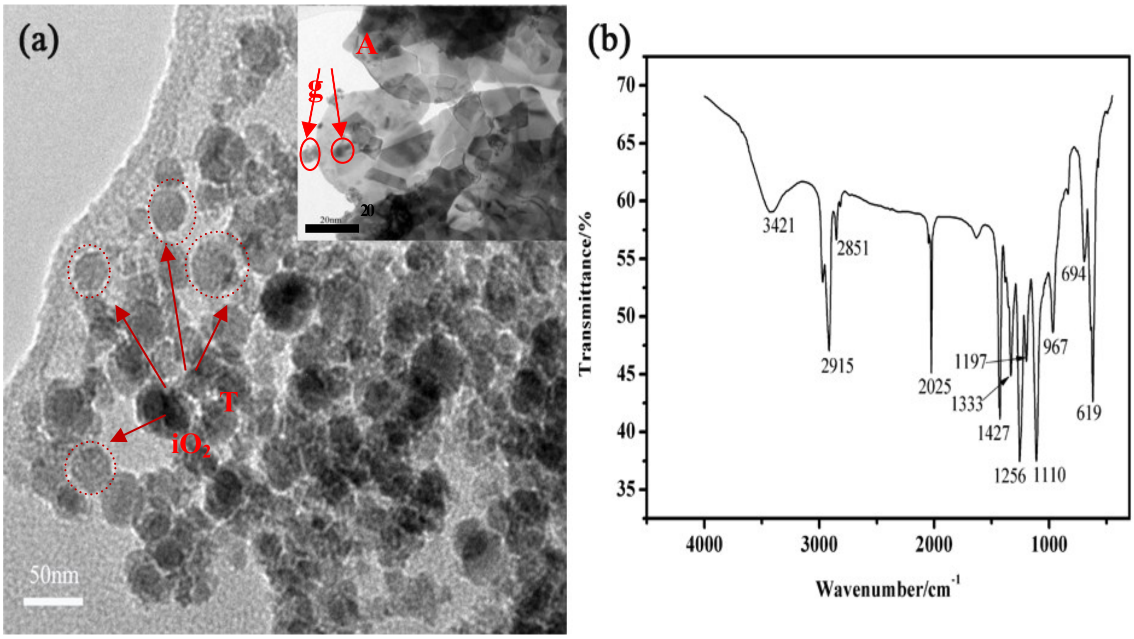

Fig. S3 TEM image (a) and FTIR spectra (b) of the Ag-n-TiO_2 particles

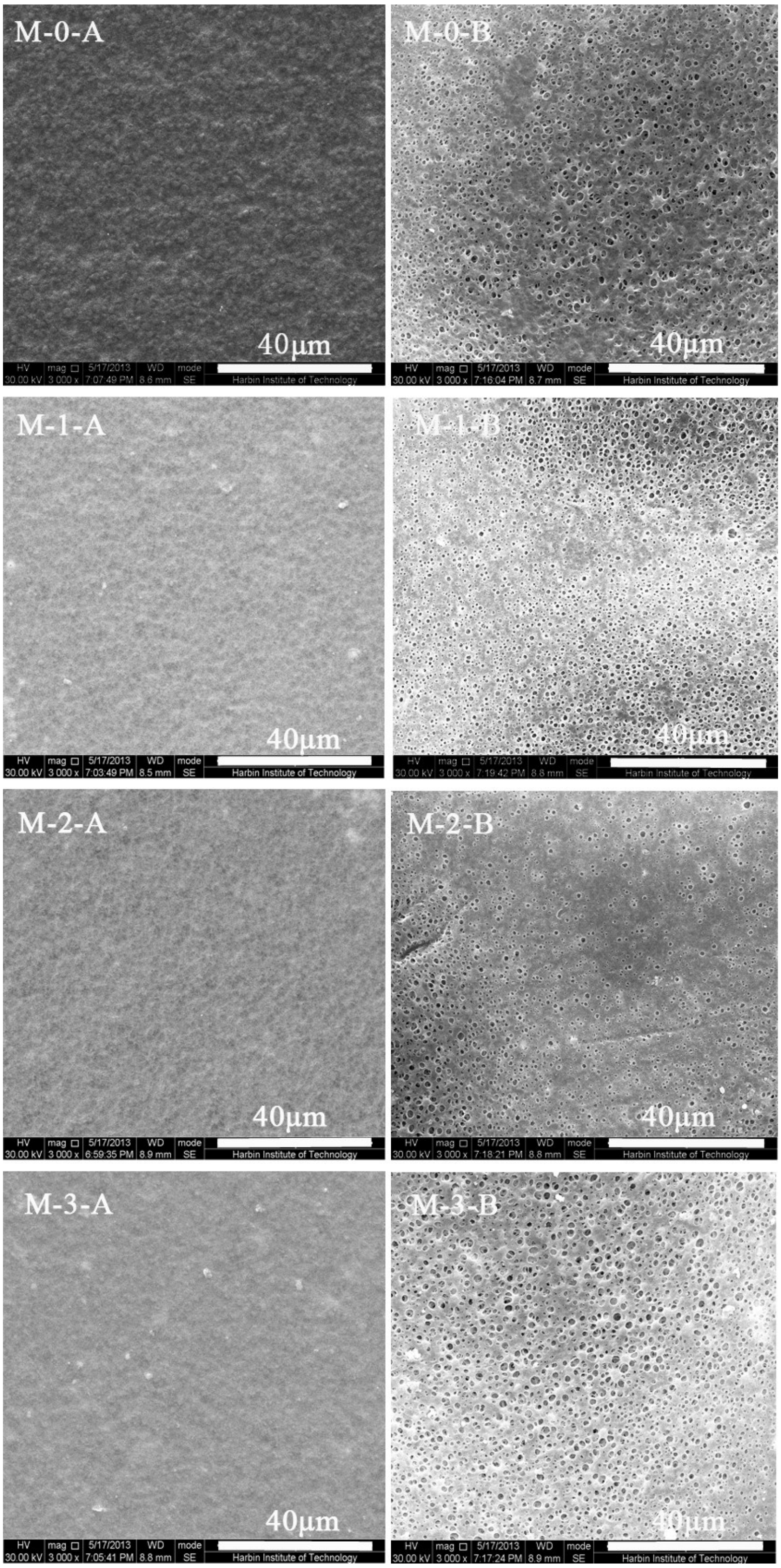

Fig. S4 SEM images for membrane of different nAg-TiO_2/PVC dosages: A for the upper surface, and B for the bottom surface. M-0 is the control sample, while M-1, M-2, and M-3 were SEM images for the membrane modified with 0.5 wt%, 1.0 wt%, and 1.5 wt% Ag-n-TiO_2, respectively

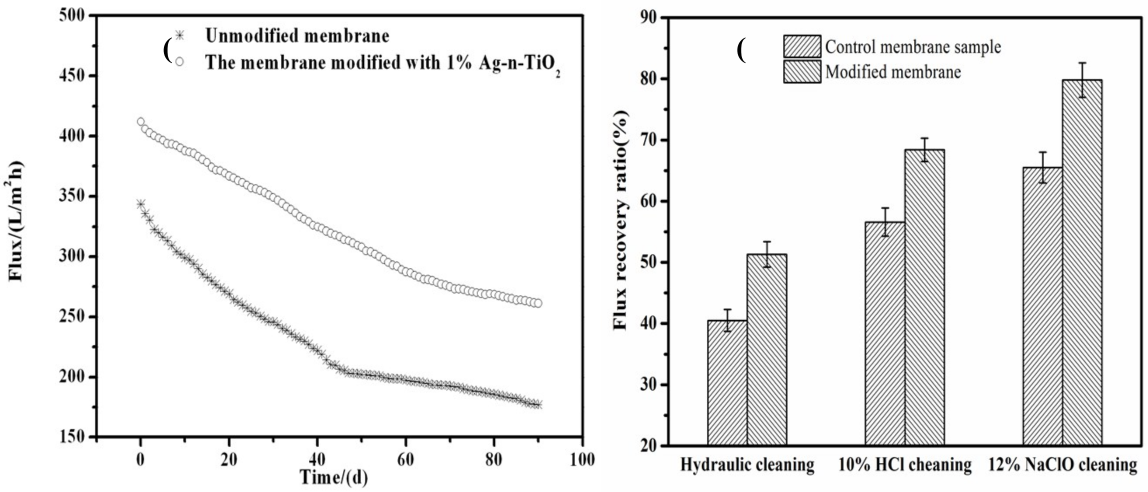

Fig. S5 (a) The permeation fluxes variation of the different membranes in the long-term filtration process, (b) Flux recovery ratios after washing with different kinds of cleaning solution, the direction of the cleaning process is opposite to the direction of filtering and all the cleaning time is 30 min.

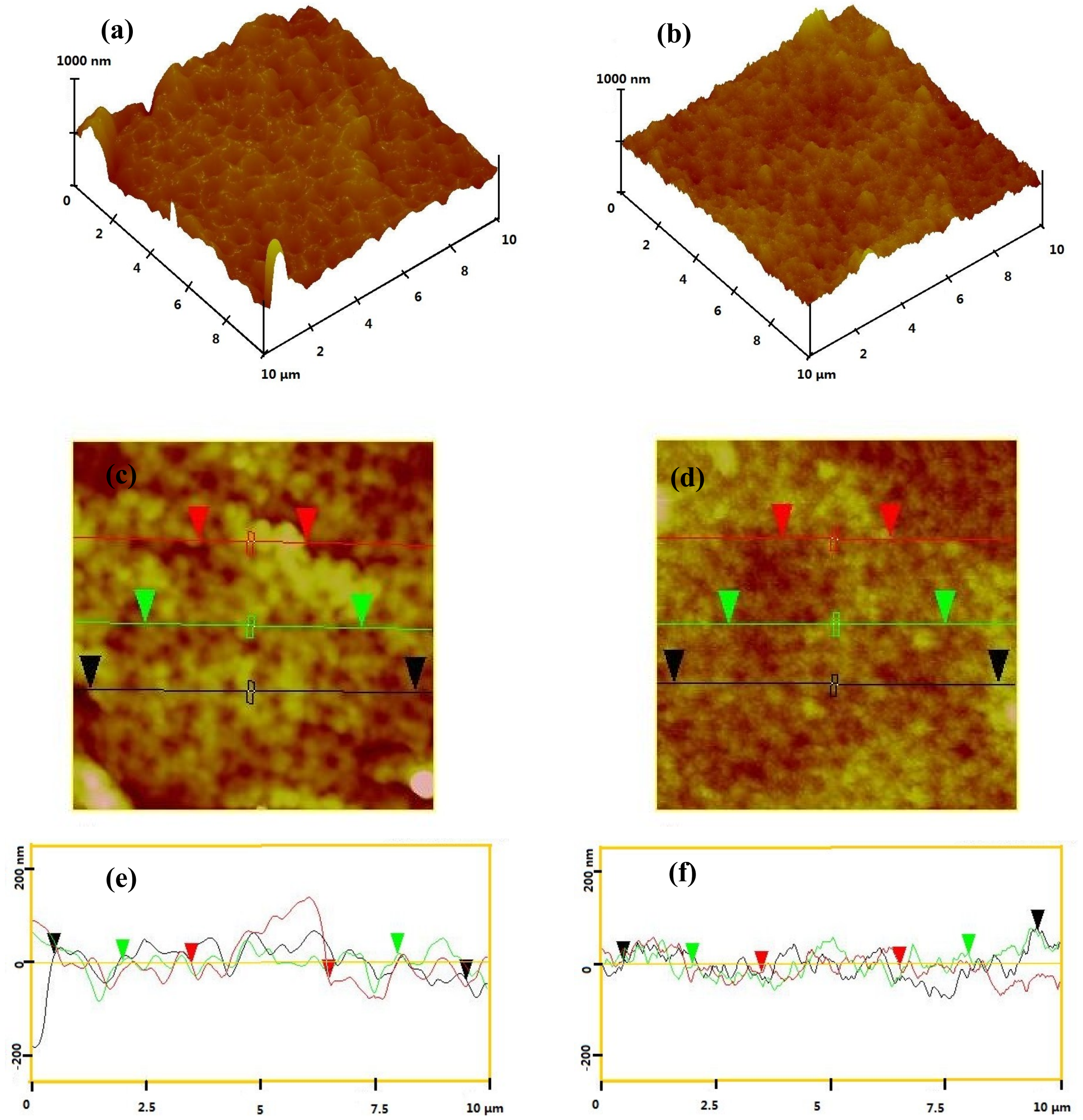

Fig. S6 Three dimensional (3D) AFM images of control membrane (0 wt % Ag-n-TiO_2) (a) and Ag-n-TiO_2/PVC membrane (1.0 wt % Ag-n-TiO_2) (b); Ridge–valley structure analyses of control membrane (0 wt % Ag-n-TiO_2) (c) and Ag-n-TiO_2/PVC membrane (1.0 wt % Ag-n-TiO_2) (d); 2D AFM surface images of control membrane (0 wt % Ag-n-TiO_2) (e) and Ag-n-TiO_2/PVC membrane (1.0 wt % Ag-n-TiO_2) (f)

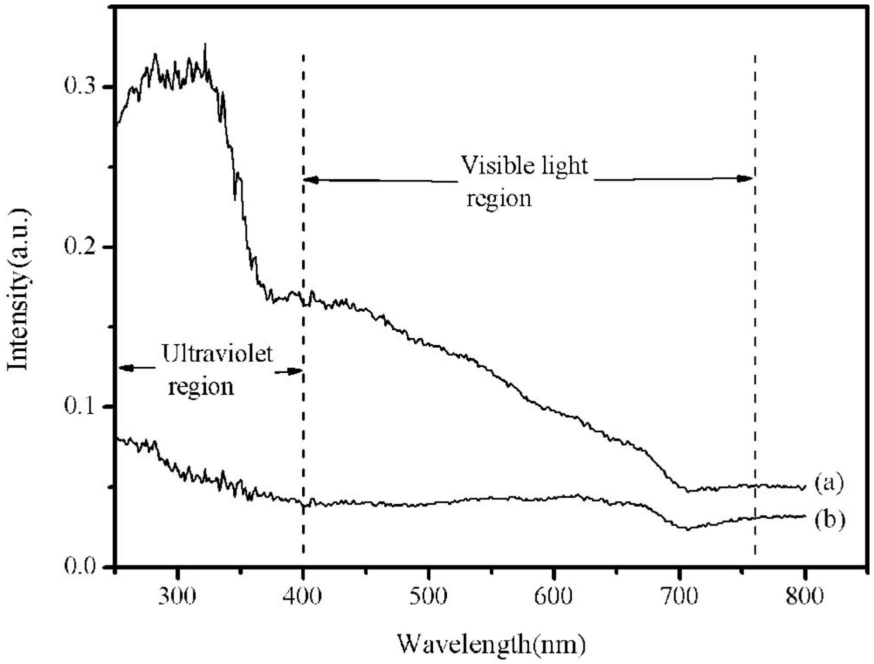

Fig.S7 Photoluminescence (PL) spectra of (a) Ag-n-TiO_2/PVC membrane (b) unmodified membrane sample

In order to investigate the photo-catalytic properties of different membranes, UV-vis absorbance measurements were conducted by UV-Vis spectrophotometer (UV-2450, Shimadzu Corporation, Japan). The membrane was fixed on the film sample holder and the reference sample was $BaSO_4$. The result was recorded in the wavelength of 200 nm–800 nm.

Fig. S7 showed the comparison UV–visible absorption spectra of unmodified PVC membrane and Ag-n-TiO_2/PVC membrane. Compare with the control sample, absorbance intensity of the Ag-n-TiO_2/PVC membrane increased in both ultraviolet and visible light regions. This implies that the addition of Ag-n-TiO_2 particles increased absorption of both UV and visible light of the modified membrane [1].

Analysis of silver and titanium ion loss

To evaluate the release of silver and titanium during the filtration process, permeate samples were collected at different time, and the volumes of the each sample were recorded. Silver concentrations in the collected samples and the residual silver content in the membranes were analyzed by an inductive coupled plasma-mass spectrometer (ICP-MS, Agilent, model 7500 CX) [2-3]. To measure total silver content in the unmodified membrane module and the module after three months filtration, the membrane was digested by sonication in 2% HNO_3 (Branson Ultrasonic 5510; Danbury, CT) for 3 days. After digestion, the suspension was filtered through a 1mm-pore-size glass fiber filter (Gelman, Type E) to remove large particles, and analyzed for total silver content [3].

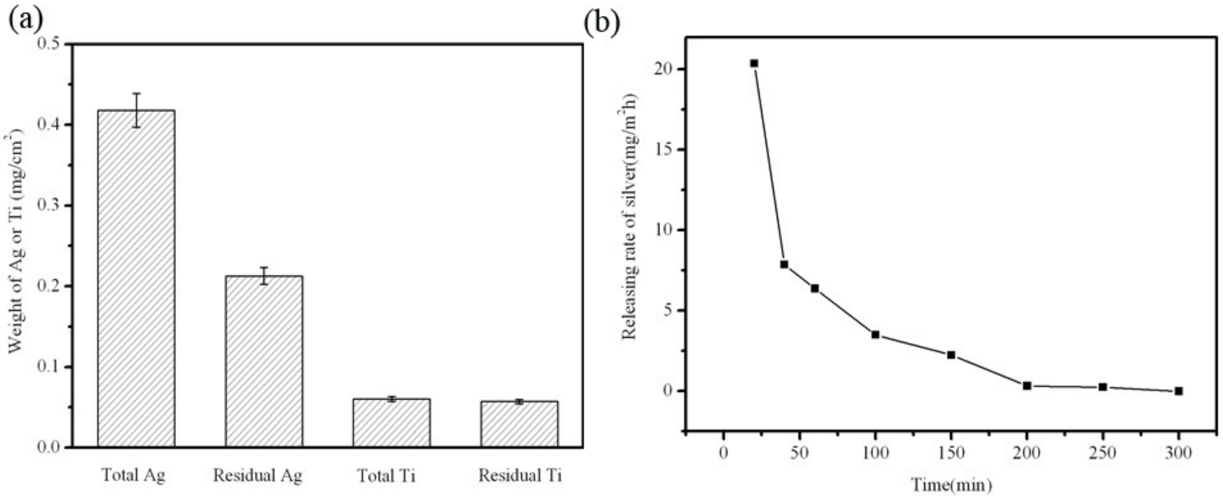

Fig. S8 Release of silver and titanium ion from the membrane in the three months of filtration (a) and the release rate of silver during the filtration test (b)

As depicted in Fig. S8 (a), the total Ag decreased 49.1% and the total Ti only decreased 5.2% in the long-term filtration process. Meanwhile, the content of Ti was lower compare with its dose amount for its low solubility at low pH in the acidic solution. In addition, the silver concentration was relatively high in the filtrate during the first 20 min, and then decreased dramatically after 60 min (Fig. S8 (b)). The released silver concentration was much lower after 200 min of filtration and was not detected after 300 min of continuous filtration process. In addition, we analyzed the release rate of titanium ion along with the silver. However, titanium concentration was lower than the detection limit of the ICP-MS instrument, indicating the extreme low solubility of Ti in aqueous solution.

Hence, TiO_2 can be applied as an effective carrier of Ag to reduce the silver release during membrane fabrication and keep its long-term antibacterial property.

References:

[1] L. Liu, Z. Liu, H. Bai, D.D. Sun, Concurrent filtration and solar photocatalytic disinfection/degradation using high-performance Ag/TiO_2 nanofiber membrane, Water Res., 46 (2012) 1101-1112.

[2] J. Huang, H. Wang, K. Zhang, Modification of PES membrane with Ag–SiO_2: Reduction of biofouling and improvement of filtration performance, Desalination, 336 (2014), 8-17.

[3] K. Zodrow, L. Brunet, S. Mahendra, D. Li, A. Zhang, Q. Li, P.J. Alvarez, Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal, Water Res., 43 (2009), 715-723.

Table S1 Compositions of Ag-n-TiO_2/PVC reinforced hollow fiber membranes and the preparation conditions

<table>
<tr><td rowspan="3">Compositions</td><td>Membrane</td><td>DMAC (Kg)</td><td>PVP (g)</td><td>W-10 (g)</td><td>T-80 (g)</td><td>PVC (g)</td><td>Ag-n-TiO_2 (g)</td></tr>
<tr><td>Control sample</td><td>2.364</td><td>303</td><td>30</td><td>46</td><td>500</td><td>0</td></tr>
<tr><td>Modified membrane</td><td>2.364</td><td>303</td><td>30</td><td>46</td><td>500</td><td>30</td></tr>
<tr><td colspan="2" rowspan="4">Membrane preparation conditions</td><td colspan="2">Agitated temperature</td><td>65 °C</td><td colspan="2">Agitated speed</td><td>40 r/min</td></tr>
<tr><td colspan="2">Soaking bath temperature</td><td>50 °C</td><td colspan="2">Coagulation bath temperature</td><td>60 °C</td></tr>
<tr><td colspan="2">Metering pump speed</td><td>10 r/min</td><td colspan="2">Length of the air bath</td><td>15 cm</td></tr>
<tr><td colspan="2">Braidd tube release speed</td><td>15 r/min</td><td colspan="2">Wire winding Wheel speed</td><td>12 r/min</td></tr>
</table>

Table S2 Water quality [a] of raw water and UF filtrates

Parameter	Raw water	Unmodified membrane		Modified membrane	
		Beginning	After fouling	Beginning	After fouling
UV_{254} (cm^{-1})	0.088±0.004	0.061±0.003	0.037±0.002	0.057±0.003	0.042±0.002
NH_4^+-N (mg/L)	0.577±0.029	0.460±0.023	0.163±0.008	0.424±0.021	0.175±0.009
TP (mg/L)	0.096±0.005	0.053±0.003	0.029±0.001	0.049±0.002	0.037±0.002
Turbidity (NTU)	0.87±0.11	0.15±0.04	0.08±0.02	0.13±0.03	0.08±0.01
pH	8.23±0.07	7.87±0.05	7.88±0.03	7.85±0.04	7.86±0.02
Fe (mg/L)	0.3412±0.0171	0.1689±0.0084	0.0076±0.0004	0.1327±0.0066	0.0088±0.0004
Al (mg/L)	0.1542±0.0077	0.1141±0.0057	0.0554±0.0028	0.0922±0.0046	0.0643±0.0032
Cu (mg/L)	0.0087±0.0004	0.0069±0.0003	0.0046±0.0002	0.0065±0.0003	0.0054±0.0003
Mn (mg/L)	0.0283±0.0014	0.0139±0.0007	0.0105±0.0005	0.0125±0.0006	0.0110±0.0006
Zn (mg/L)	0.1926±0.0096	0.1085±0.0054	0.07017±0.0036	0.1005±0.0050	0.0087±0.0044
Total bacterial count (CFU/mL)	67±11	2±1	ND [b]	2±1	ND [b]

[a] The Water quality analyses in Table S2 were conducted on the basis of Chinese National Standard methods (GB/T5750.3-2006, China). Specifically, the UV absorbance at 254 nm (UV_{254}) of 0.45 μm filtered solutions was determined by an ultraviolet/visible spectrophotometer (TU-1810, Beijing Purkinje Genera, China). Residual iron, manganese, copper, aluminum, zinc after 0.45 μm membrane filtration were analyzed by an inductive coupled plasma mass spectrometer (ICP-MS, Agilent, model 7500 CX). Turbidimetric analysis was analysed by a turbidimeter (PHS-3C, Shanghai mine magnetic instruments factory). The concentration of NH_4^+-N and NO_3 was determined by the colorimetric method using a spectrometer by Chinese National Standard methods.

[b] ND was mean no detection.

Table S3 Surface roughness data of unmodified and modified membranes

Membrane	Scanning area	Total surface area (μm^2)	Roughness		
			R_{ms} (nm)	R_a (nm)	R_{max} (nm)
Control sample	10 μm × 10 μm	100.287	57.004	24.268	199.62
Ag-n-TiO_2/PVC	10 μm × 10 μm	100.115	19.494	12.286	66.972