



Self-cleaning and antifouling polyvinylidene difluoride hollow fiber membrane enabled by visible light irradiation for water treatment

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ABSTRACT

A polydopamine (PDA) layer was attached onto the surface of a polyvinylidene difluoride hollow fiber membrane via the self-polymerization of the dopamine. Amine-functionalized N-TiO₂ (N-TiO₂-NH₂) nanoparticles were covalently bound with the PDA layer via amine-catechol adduct formation. N-TiO₂ anchored onto the membrane surface could be activated by visible light irradiation, thus imparting the membrane's self-cleaning activities. The coating method enhanced the contact area between photocatalytic particles and contaminants when compared to the membrane fabricated by the blending method. In comparison with ultraviolet (UV) light irradiation, the application of visible light irradiation could save energy and prevent membranes from deterioration. The membranes were characterized by scanning electron microscopy and their performances were evaluated based on the water permeability, humic acid (HA) rejection and antifouling property. Under visible light irradiation, the pure water flux of the membrane modified with (N-TiO₂-NH₂) (NTN) via dopamine could recover 100% of its original flux in the second day. The antifouling property of membranes modified with NTN could be further increased by UV irradiation; however, the UV light might deteriorate quickly the modified layer on the membrane surface. These results demonstrated that the methodology developed here was capable of preventing membrane fouling and cleaning the fouling surfaces. An important advantage using visible light irradiation is its relatively low energy costs and minimal deterioration of the membrane structure.

Keywords: Hollow fiber membrane; Membrane fouling; Photocatalysis; Ultrafiltration; Polyvinylidene difluoride

1. Introduction

Polyvinylidene difluoride (PVDF), a semi-crystalline polymer, has a crystalline phase and an amorphous and/or rubbery phase. The crystalline phase endows thermal stability and the amorphous phase flexibility, both are desirable characters of quality membranes [1]. PVDF has been used to fabricate microfiltration, ultrafiltration, and nanofiltration membranes with excellent chemical resistance, high thermal

stability, good mechanical properties, and good membrane forming ability [2–4]. However, its efficiency in water treatment applications is often affected by the membrane fouling, as PVDF can easily attract organic compounds because of its inherently low surface energy. The fouling issue may cause severe water flux decline, shortened membrane life, and increased operation cost [5–7]. Much effort has been devoted to fouling alleviation and membrane cleaning including pre-treatment of the feed solution, optimization of filtration

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conditions, and membrane cleaning. However, the complexity of the operating process and cost are increased by these fouling-control strategies. Modification of a membrane is another approach to address the membrane fouling issue, especially, by introducing hydrophilic additives to the membrane surface [8,9]. Many studies have attempted to improve the PVDF membrane performances by blending and surface coating of various polymers and particles [10–14]. The blending method can be easily adapted for the common phase inversion method for membrane fabrication; however, the entrapped additives are not fully exposed to the membrane surfaces because of the blockage of the primary PVDF polymer. In contrast, the surface coating could maximize the contact area between the feed solution and hydrophilic surface additives.

Recent studies of PVDF modifications have focused on incorporating polymers with inorganic materials [15–17]. Inorganic nanoparticles that could be blended with polymer membranes include silica (SiO_2), alumina (Al_2O_3), ferrous ferric oxide (Fe_3O_4), zinc oxide (ZnO), zirconium oxide (ZrO_2), graphene oxide (GO), and titanium dioxide (TiO_2) [18,19]. Among various inorganic additives, TiO_2 has received the most attention because of its stability, photocatalytic property, availability, and low to non-toxicity. Its wide band-gap (3.2 eV for anatase polymorph) and high recombination rate of photo-induced charge carriers partially hinder its practical application [20]. High energy input [ultraviolet (UV) light] was required for activation, hence making TiO_2 relatively costly for applications. For the sunlight reaching the earth's surface, TiO_2 could only utilize <5% of the irradiation, which is in the UV range [21]. To extend the range where TiO_2 could be applied for environmental applications, numerous attempts have been dedicated to making TiO_2 sensitive to visible light irradiation, hence solar light could be efficiently utilized. The approaches explored include noble dye sensitization [22], metal deposition [23], and metal or non-metal doping [24,25]. Among various non-metal doping materials, N-doped TiO_2 is among the best-studied due to its high efficiency under visible light irradiation, probably because of the mixing of N 2p states with O 2p states, as their energy levels are very close [26].

To coat TiO_2 onto the membrane, it is desirable to link the membrane surface with TiO_2 via chemical binding. Dopamine is considered an excellent coupling ligand to bind TiO_2 with organic materials. It is known that TiO_2 nanoparticles could be easily immobilized on the surface of the polydopamine (PDA) spheres with strong coordination bonds and hydrogen bonds under mild conditions [27]. A strong bidentate complex can be formed at the surfaces of nanoparticles because two OH groups in the ortho position of enediol ligands can bind firmly with the unsaturated Ti atoms. Feng et al. [28] reported amine-functionalized TiO_2 ($\text{TiO}_2\text{-NH}_2$) nanoparticles were chemically bonded with the PDA layer via amine-catechol adduct formation. Dopamine was also known to self-polymerize on most materials surfaces due to its multifunctional groups (amino and catechol groups) [29]. We, therefore, hypothesize that a surface coating of N-doped TiO_2 could be constructed using dopamine as a linker.

In this work, we explored if amine-functionalized N-doped TiO_2 nanoparticles, which can be activated under visible light irradiation, could be grafted onto the PVDF

membrane surfaces using dopamine as a linker. The surface-coated membranes with amine-functionalized N-doped TiO_2 were evaluated in terms of their filtration performance and antifouling characteristics under both visible light and UV light irradiation conditions.

2. Materials and methods

2.1. Materials

PVDF (MW 180,000 Da), N-Methyl-2-pyrrolidone (NMP; anhydrous, 99.5%) and polyvinylpyrrolidone (PVP; 10,000 Da) were obtained from Sigma Aldrich (St. Louis, US) and used for the preparation of membranes. Tris(hydroxymethyl) amino-methane (99.8+%) (Tris) and 3-(3,4-dihydroxyphenyl)-L-alanine 3-aminopropyltriethoxysilane (APS) were purchased from Sigma Aldrich. Tetrabutyl titanate [$\text{Ti}(\text{OBU})_4$, 97%, Aldrich] and ammonia aqueous solution (28–30%, Aldrich) were used as titania precursor and nitrogen source to the synthesis of N- TiO_2 NPs, respectively. Dopamine hydrochloride was provided by Sigma Aldrich.

2.2. Synthesis and characterization of N- TiO_2 NPs

A method published in the previous study was applied with modification for the synthesis of N- TiO_2 NPs [30]. Twenty milliliters of $\text{Ti}(\text{OBU})_4$ solution was mixed with 10 mL ammonia aqueous solution at 25°C with vigorous stirring for hydrolysis. After 20 min stirring, the precursor was dried in an oven at 110°C for 3 h and then calcinated at 400°C for 1 h to obtain N- TiO_2 NPs.

2.3. N- $\text{TiO}_2\text{-NH}_2$ (NTN) Preparation

The preparing method of N- $\text{TiO}_2\text{-NH}_2$ was adopted from literature reports [28]. One hundred and fifty milliliters of absolute ethanol were applied to disperse 760 mg N- TiO_2 and the mixture was ultrasonicated for 10 h to obtain a brown and homogeneous suspension. Then, the dropwise addition of APS solution (1 g APS dissolved in 50 mL absolute ethanol) to the N- TiO_2 colloidal suspension was applied. The mixture was refluxed at 80°C for another 6 h, then centrifuged to obtain the N- TiO_2 product. Absolute ethanol was used to thoroughly wash the product. The product was dried in oven at 40°C prior to use.

2.4. Membrane fabrication

The dope solution for making the membrane was prepared by dissolving PVDF (9.6 g) and PVP (3 g) in NMP (47.4 g) under the heating and stirring at 60°C for 8 h. Prior to spinning, the dope solution was cooled and left for 12 h to eliminate bubbles. The hollow fiber membrane (HFM) was prepared with the dope solution via a phase inversion method. The prepared dope solution and bore liquid were simultaneously driven through a spinneret. A hollow fiber was shaped while the dope solution entered the coagulation bath containing tap water. The dimensions of the spinneret were designed at 1,000 μm as outer diameter (OD) and 600 μm as inner diameter (ID). A constant rate was set to collect the fibers. After collecting, deionized (DI) water was used to thoroughly wash the fibers. A schematic

representation for fabricating and modifying the HFM is shown in Fig. 1. The spinning conditions are listed in Table 1.

2.5. Preparation of PDA/PVDF and NTN/PDA/PVDF composite HFMs

Firstly, 0.2 wt% dopamine buffer solution (Tris-HCl, pH 8.5) was used to soak the PVDF HFMs for 15 min or 30 min. Then, the HFMs were rinsed with ethanol and DI water for three times to remove any loosely bound dopamine. Then, ethanol in the membrane was exchanged with DI water for at least 30 min. These membranes were named based on soaking time as “PVDF 15PDA” and “PVDF 30PDA,” respectively. 0.05 wt% NTN Tris-HCl buffer solution (Tris-HCl buffer solution, pH = 8.5) was used to soak the prepared membranes at 35°C for 2 h [28]. These membranes were named as “PVDF 15PDA-NTN,” “PVDF 30PDA-NTN,” respectively. The NTN/PDA/PVDF composite membranes were rinsed with DI water for further evaluation.

2.6. Membrane characterization and performance assessment

The morphology of the HFM surface was tested by a high-resolution scanning electron microscope (ZEISS, MERLIN, Germany). The membrane water flux and solute rejection was tested by a cross-flow filtration system. A schematic diagram of measuring permeate flux through the HFM is shown in Fig. 2. Before each test, the membrane was compacted by DI water at 7 psi for 2 h. The permeating flux was evaluated by weighting the amount of permeate solution as a function of time, which was achieved by using a LabVIEW automated system (National Instruments LabVIEW 2014 with Ohaus digital balance). The flux and rejection were calculated based on Eqs. (1) and (2), respectively.

$$J = \frac{V_p}{A \times t} \quad (1)$$

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

Here J (L/m²h) is the flux of permeate solution, V_p (L) is the permeate volume, A (m²) is the membrane area, t (h) is the filtration time, and R is the rejection ratio. C_p and C_f are the concentrations of permeate and feed solution, respectively. Ultraviolet-visible spectrophotometry at 254 nm was used to determine the humic acid (HA) concentration. Feed solution and permeate solution were collected after light irradiation for the characterization of membrane rejection.

Characterization of membrane fouling properties was determined by cyclic membrane filtration tests in this study. Briefly, after a certain period of compaction, the membrane was evaluated with DI water for 0.5 h, and then 20 mg/L HA solution was used replacing the DI water as the feed for 3 h.

Table 1
Spinning conditions of PVDF HFMs

Parameter	Condition
Spinneret OD/ID	1.0/0.6 mm
Spinneret temperature (°C)	25
Dope solution	PVDF/PVP/NMP
Concentration (wt.%)	16/5/79
Dope solution flow rate (mL/min)	2.0
Bore fluid composition	DI water
Bore fluid flow rate (mL/min)	0.8
Coagulant	Tap water
Coagulant temperature (°C)	25
Range of air-gap distance (cm)	0
Washing bath	Tap water
Washing bath temperature (°C)	25
Take-up speed (cm/min)	240

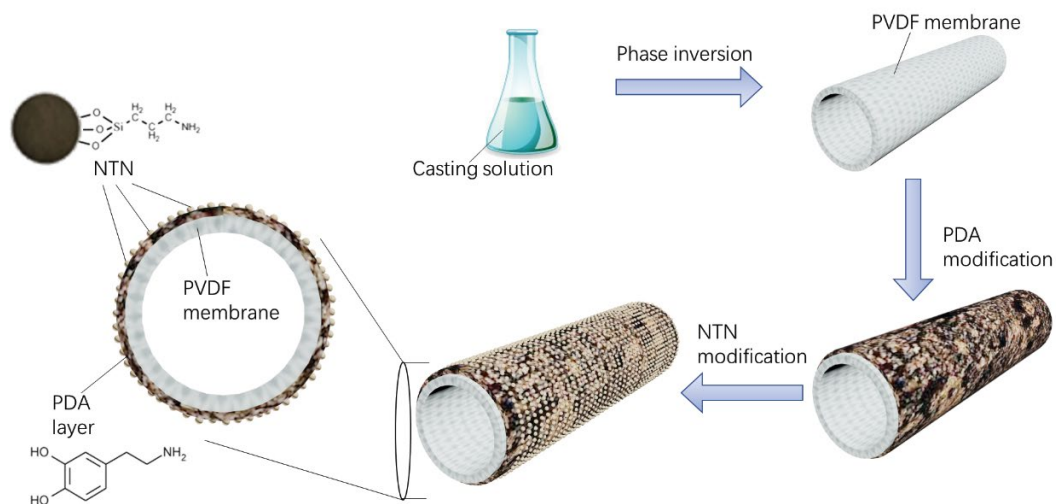


Fig. 1. Schematic representation for fabricating and modifying the HFM.

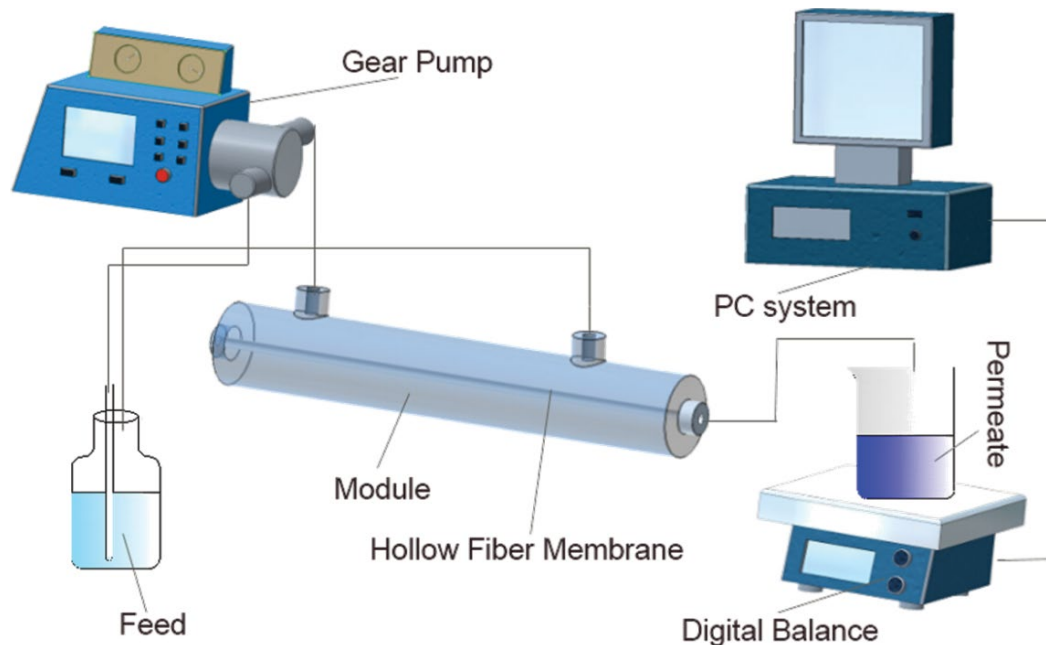


Fig. 2. Schematic diagram of measuring permeate flux through the HFM.

After washing with pure water, the membrane was tested with DI water as a feed again for another 0.5 h, completing one cycle. In the second cycle, HA was used as the feed again for 3 h of filtration, followed by DI water as feed for 30 min. Afterward, the membrane was placed with or without light irradiation for 12 h. On the second day, the membrane filtration was conducted with DI water for 30 min.

UV light (602654 LPHO, 13.1 mW/cm², Trojan Technologies, Canada) was applied for the photocatalytic irradiation. Simulation of the sunlight was achieved by four full-spectrum fluorescent light tubes (32 W, Philips F32T8) to activate the photocatalytic membranes. All the spectrum information on the light sources can be obtained from our previous work [14,31].

3. Results and discussion

The surface morphologies of the PVDF membrane and modified membranes are shown in Fig. 3. The pristine PVDF membrane presented the smoothest surface. Loose and relatively rough structures of the membrane surface was endowed by dopamine coating. The nanoparticle coating was not very uniform due to the coagulation of the nanoparticles. When the PDA layer contacted TiO₂ nanoparticles, the membrane surface became connected with the TiO₂ and dopamine grew around the TiO₂ nanoparticles. Generally, when the PDA-modified membrane contacted the TiO₂ suspension, the TiO₂ nanoparticles were immediately attracted by the catechol/quinone groups on the PDA surface [32]. Since the aqueous environment was basic, nanoparticles and the membrane surface could further react with the residual dopamine monomers.

The pure water fluxes of PVDF HFMs are presented in Fig. 4. The water fluxes overall fell within a narrow range from 150 to 200 L/m²/h. The membrane modified with

dopamine showed a lightly lower flux than that of the pristine PVDF membrane, and the introduction of NTN onto the membrane surface decreased the water flux 10%–30%. It's understood that the membrane surface and pores, when covered by dopamine, increased membrane resistance [28,33]. Hence, the membrane flux was decreased. The data here further showed that the addition of NTN on the membrane further hindered the water passage due to the coverage of membrane pores, although the magnitude of the impact was relatively small.

Fig. 5 shows the HA rejection of various HFMs with and without modification in the presence and absence of light. For the original PVDF membrane, there was no major difference in HA rejection with/without light irradiation, regardless of the used light being UV or visible light. The reject was ~80% in the first cycle and increased to 84% for the second cycle. For the dopamine-modified membranes with NTN, the rejections were improved under visible light irradiation to 88%–92%, however, no obvious improvement was observed under UV light irradiation in comparison with the pristine membranes. It is unclear why under the visible light irradiation the rejection is slightly higher but not under the UV for the membranes with NTN. A plausible explanation is the additional dopamine polymerization under the visible light that has enhanced HA rejection. Under high energy UV irradiation, the dopamine layer on the membrane surface could be destroyed [27], hence, some parts of NTN on the membrane surface were flushed away during the filtration process, and as a result, there was no obvious change for the rejection under UV irradiation compared with the dark condition.

HA was used as the model foulant to evaluate the fouling property of membranes under different conditions (dark, visible-, and UV-light). Fig. 6 shows the fouling behaviors of the PVDF membrane under various conditions. PVDF

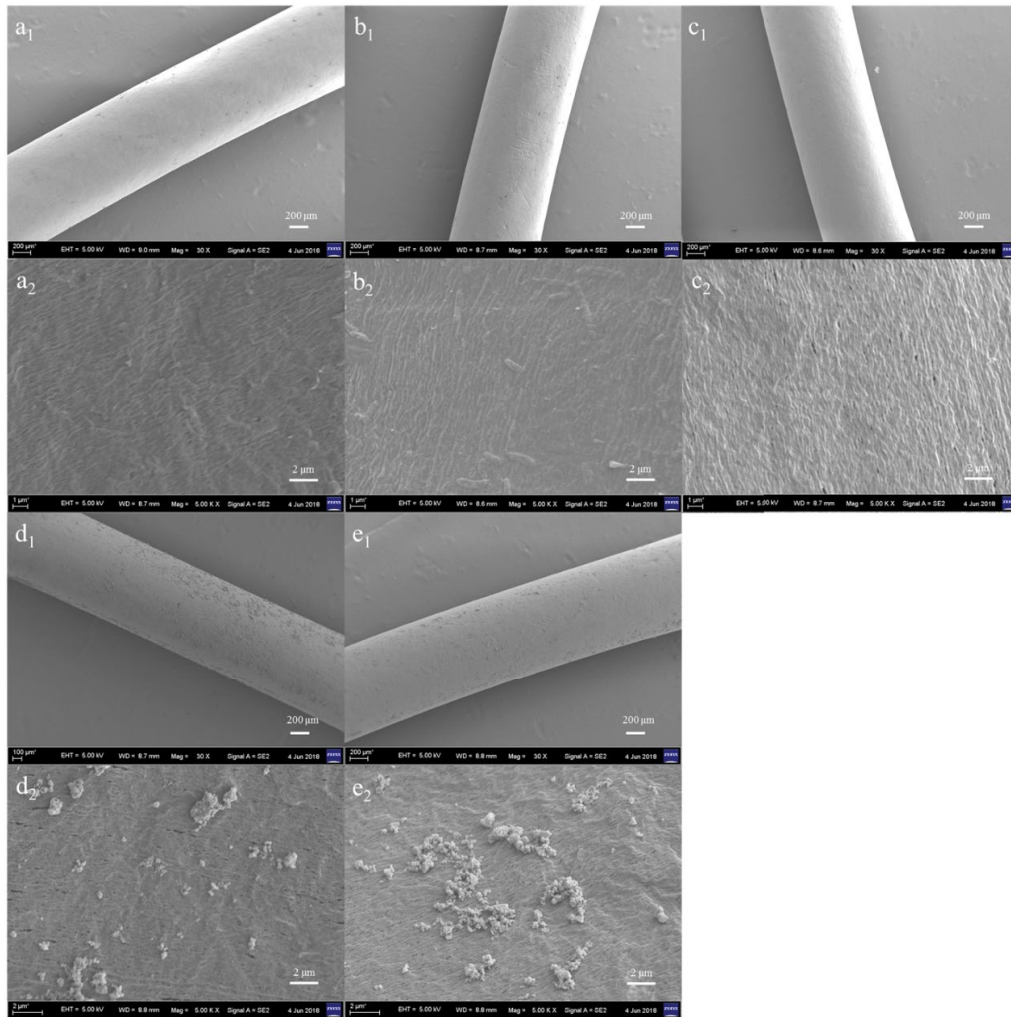


Fig. 3. Scanning electron microscopy images of HFMs (scale bar 1: 200 μm ; 2: 2 μm): (a) PVDF, (b) PVDF 15PDA, (c) PVDF 30PDA, (d) PVDF 15PDA-NTN, and (e) PVDF 30PDA-NTN.

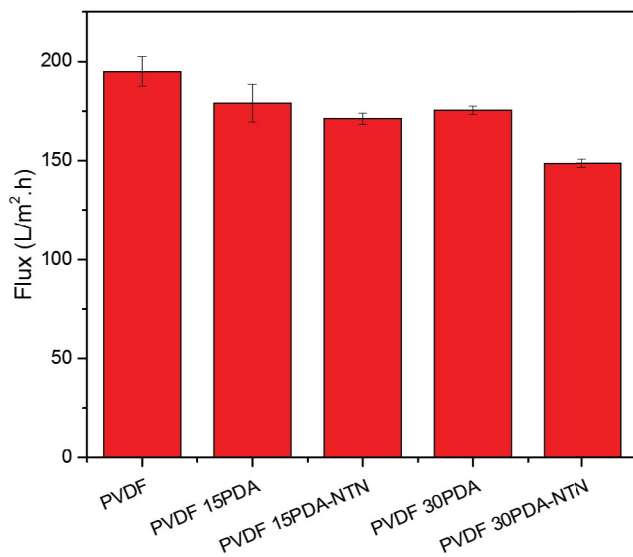


Fig. 4. Pure water fluxes of PVDF HFMs.

membrane presented similar fouling tendency under visible light irradiation and dark condition. The relative flux was improved in section W_1 and section W_2 for the PVDF under UV light irradiation. The improved flux in section W_1 under UV might be caused by the oxidation of the PVDF membrane surface, so the surface OH functional group could be created, thus improving the membrane hydrophilicity and water flux [28]. In section W_2 , HA residues could be degraded by UV light so the water flux could be fully recovered after HA fouling.

Fig. 7 shows the antifouling performance of PVDF 15PDA-NTN under various conditions (dark, visible-, and UV-light). The antifouling performance of PVDF 15PDA-NTN under visible light and UV light irradiation were better than that in dark condition. In section W_2 , the pure water flux of membrane was fully recovered to original flux under the visible light irradiation and the relative flux reached around 120% under UV light irradiation. The excellent antifouling performance under visible light irradiation could be attributed to the improved surface hydrophilicity by NTN and degradation of the HA on the membrane

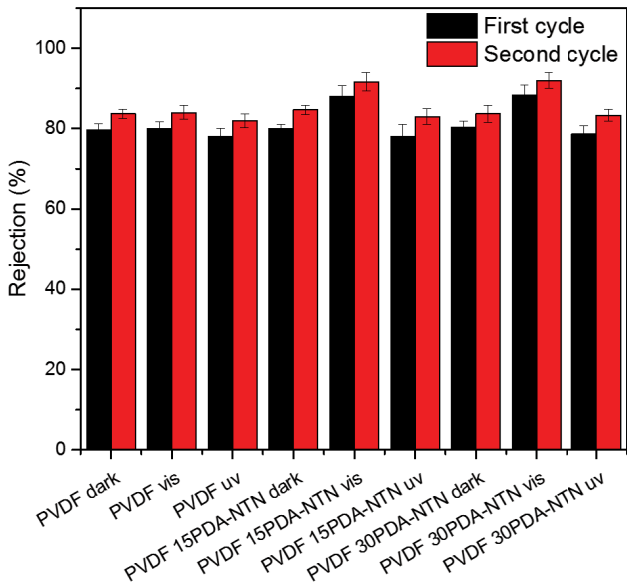


Fig. 5. Humic acid rejection of the PVDF HFM and modified HFMs.

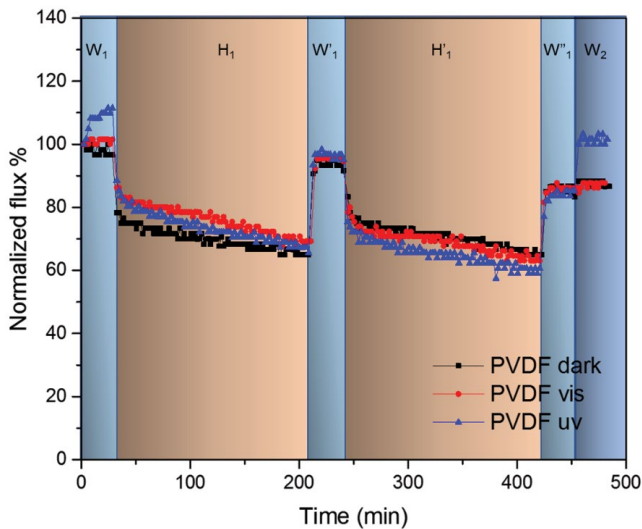


Fig. 6. Antifouling performance of PVDF membrane under dark condition, visible light irradiation, and UV irradiation. Section “W” refers to that the operation solution is pure water, while “H” shows that the feed solution is 20 mg/L HA (pH = 7). The number behind the letter “W/H” is the cumulative days of visible light irradiation.

surface. Under the UV light irradiation, HA on the membrane surface could be degraded. The modified dopamine layer and even the PVDF membranes might be partially damaged, as suggested by the observed water flux higher than the pristine membrane under UV light irradiation [34]. PVDF membrane could be damaged by the UV [35].

Fig. 8 presents the antifouling performance of PVDF 30PDA-NTN under light irradiation (visible- and UV-light)

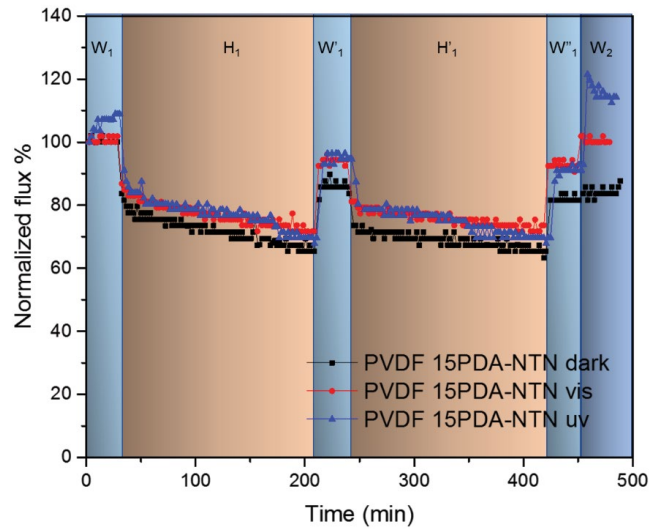


Fig. 7. Antifouling performance of PVDF 15PDA-NTN membrane under dark condition, visible light irradiation, and UV irradiation.

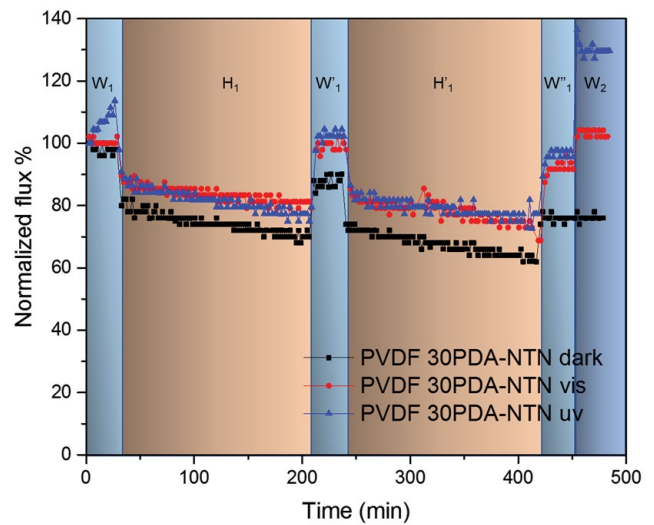


Fig. 8. Antifouling performance of PVDF 30PDA-NTN membrane under dark condition, visible light irradiation, and UV irradiation.

and dark condition. The membrane demonstrated a better antifouling property under the light irradiation (visible- and UV-light) when compared with the dark condition. On the second day, the pure water flux of the membrane was recovered to 100% under visible light irradiation and reached 130% under UV light condition. Compared to PVDF 15PDA-NTN, PVDF 30PDA-NTN showed higher water flux recovery under UV light irradiation likely due to the more hydrophilic NTN on the membrane surface [28]. The NTN on the membrane surface became more hydrophilic and could degrade HA during the filtration process under either visible light or UV light irradiation [14,31]. However, the UV light could further deteriorate the dopamine layer

modified on the membrane surface, which is believed to have caused further enhancement of flux on the second day.

4. Conclusions

NTN was successfully anchored onto the membrane surface by using dopamine layer as a linker. HA rejection was improved for the membrane modified with NTN under visible light irradiation. The pure water flux of the membrane modified with NTN could recover to 100% of its original flux under visible light irradiation. The improved antifouling behavior under visible light irradiation could be attributed to the improved surface hydrophilicity imparted by NTN and the activated NTN that could degrade HA on the membrane surface. Even though the antifouling performance could be improved under UV light irradiation, the membrane flux has increased to a level significantly higher than the original membrane, suggesting that the membrane surface might have been damaged by the catalytic oxidation of HA and membrane surface under the UV light irradiation. Compared to UV light irradiation, visible light irradiation is more practical for the photocatalytic membrane application.

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