

Thermo-responsive and Antifouling PVDF Nanocomposited Membranes Based on PNIPAAm Modified TiO₂ Nanoparticles^{*}

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Abstract A novel hydrophilic nanocomposite additive (TiO₂-g-PNIPAAm) was synthesized by the surface modification of titanium dioxide (TiO₂) with *N*-isopropylacrylamide (NIPAAm) via “graft-from” technique. And the nanocomposite membrane of poly(vinylidene fluoride) (PVDF)/TiO₂-g-PNIPAAm was fabricated by wet phase inversion. The graft degree was obtained by thermo-gravimetric analysis (TGA). Fourier transform infrared attenuated reflection spectroscopy (FTIR-ATR) and X-ray photoelectronic spectroscopy (XPS) characterization results suggested that TiO₂-g-PNIPAAm nanoparticles segregated on membrane surface during the phase separation process. Scanning electron microscopy (SEM) was conducted to investigate the surface and cross-section of the modified membranes. The water contact angle measurements confirmed that TiO₂-g-PNIPAAm nanoparticles endowed PVDF membranes better hydrophilicity and thermo-responsive properties compared with those of the pristine PVDF membrane. The water contact angle decreased from 92.8° of the PVDF membrane to 61.2° of the nanocomposite membrane. Bovine serum albumin (BSA) static and dynamic adsorption experiments suggested that excellent antifouling properties of membranes was acquired after adding TiO₂-g-PNIPAAm. The maximum BSA adsorption at 40 °C was about 3 times than that at 23 °C. The permeation experiments indicated the water flux recover ratio and BSA rejection ratio were improved at different temperatures.

Keywords: PVDF membrane; TiO₂-g-PNIPAAm nanoparticle; Thermo-responsive; Antifouling.

INTRODUCTION

Nanocomposite membranes, blending inorganic particles with polymer materials, become an emerging technology for separation and purification in recent years. This concept is an effective method to improve the performance of membranes as the blended membrane can acquire advantages of both organic and inorganic materials such as superior hydrophilicity, permeability and selectivity^[1].

Poly(vinylidene fluoride) (PVDF) is a kind of the most extensively applied organic polymer membrane material owing to the excellent thermal stability, chemical resistance and low toxicity^[2]. However, the serious protein-fouling problem had been the major drawback in the water treatment because its hydrophobicity always causes adsorption or deposition between membrane surfaces and organic foulants^[3, 4]. Recently, many researchers concern on blending PVDF with inorganic particles, such as TiO₂^[5–7], Al₂O₃^[8], ZrO₂^[9], Fe₃O₄^[10] and one dimensional TiO₂ nanowires^[11]. Among various nanoparticles, TiO₂ has received the most attention because

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of its hydrophilicity and antifouling abilities^[12, 13]. The PVDF/TiO₂ nanocomposite membrane possesses several advantages like excellent self cleaning/antifouling, bactericidal and photoactive properties based on UV/TiO₂ photocatalytic mechanism. However, TiO₂ particles are liable to aggregate in the membrane because of the huge difference between the polymer and inorganic materials in their properties and separate from the nanocomposite membrane. To overcome this issue, the improvement of compatibility between inorganic materials and the membrane is a very effective method. Razmjou *et al.*^[14] reported a novel PES nanocomposite membrane blended with modified-TiO₂ nanoparticles *via* 3-aminopropyltriethoxysilane (APTES) monomer. The experiments indicated that the structure, hydrophilicity and separation performance acquired great improvement owing to the superior dispersion of TiO₂-APTES nanoparticles in the membrane.

Stimuli-sensitive PVDF membranes have been investigated as an excellent induction to the surrounding environment. For example, temperature responsive ability can be used in smart separation membranes^[15, 16]. The thermo-responsive PNIPAAm exhibits a lower critical solution temperature (LCST) around 32 °C in aqueous medium. Chen *et al.*^[17] reported a thermo-responsive PVDF membrane prepared by blending PNIPAAm monomer with PVDF powder exhibits temperature-sensitive permeability to aqueous solutions and the enhanced antifouling ability. Hence, the TiO₂-g-PNIPAAm additive is a good solution to improve the compatibility between TiO₂ nanoparticles and PVDF in membranes. Moreover, the nanoparticles endow thermo-responsive and hydrophilic properties to PVDF membranes.

Herein, a kind of inorganic-organic nanocomposite additive (TiO₂-g-PNIPAAm) was synthesized *via* “graft-from” polymerization in the presence of 2,2'-azobisisobutyronitrile (AIBN) as the initiator. Then nanocomposite PVDF/TiO₂-g-PNIPAAm membranes were fabricated by wet phase inversion. The modified membranes showed a significant thermo-responsive property in contact angle and permeation experiments. Using BSA aqueous solution as model foulants, the separation and antifouling properties of the membranes were extensively investigated, and all the properties were correlated to the addition of TiO₂-g-PNIPAAm in PVDF matrix membranes.

EXPERIMENTAL

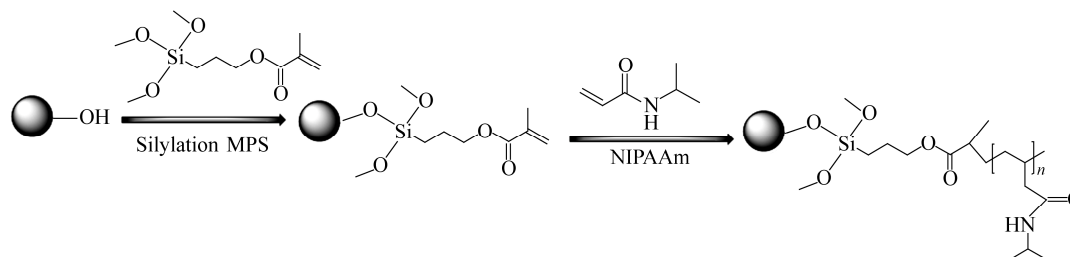
Materials and Reagents

PVDF (FR-904, $M_n = 3.8 \times 10^5$) was purchased from Shanghai 3F New Materials Co. LTD. and dried at 80 °C for 12 h before use. Titanium dioxide (TiO₂) was purchased from Hang Zhou Wan Jing Xin Materials Co. and dried before use at 100 °C in vacuum for at least 12 h. *N*-isopropylacrylamide (NIPAAm), 3-methacryloxypropyltrimethoxysilane (MPS) and bovine serum albumin (BSA, $M_n = 6.7 \times 10^4$ Da) were received from Aldrich. NIPAAm was used after purification triple by recrystallization in toluene and hexane (3/7, *V/V*) acetone and then dried in vacuo at room temperature. Polyvinylpyrrolidone (PVP), *N,N*-dimethylacetamide (DMAc), 2,2'- azobisisobutyronitrile (AIBN), ammonia (25 wt%) and absolute ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. AIBN was purified by recrystallization in ethanol before use. The phosphate buffered saline (PBS, 0.1 mol, pH = 7.4) was prepared by the addition of pre-packaged buffer salts (Aldrich) to deionized water.

Functionalization of TiO₂ Nanoparticles

The modification of TiO₂ nanoparticles with MPS and NIPAAm is shown in Scheme 1. The detailed steps were as follows. First, the TiO₂-MPS nanoparticles were synthesized. 2 g TiO₂, 2.6 g of water, 1.36 g of ammonia (25 wt%) and 1.44 g of MPS were added into 50 mL of ethanol. The mixture was under ultrasonication for 1 h and then was mechanically stirred at 700 r/min at room temperature for 48 h. The solution was purified in absolute ethanol five times. After vacuum drying for 12 h at 50 °C, the white powder of MPS modified TiO₂ (represented TiO₂-MPS) was acquired. Then, 1 g TiO₂-MPS nanoparticles, 50 mL of anhydrous ethanol, 1 g NIPAAm monomer and 0.15 g AIBN were added into a 100 mL three-necked flask fitted with a condenser and a thermometer in an oil bath. Free radical polymerization was performed at 70 °C in argon atmosphere and allowed to proceed for 24 h. After polymerization, the product was centrifuged and washed with ethanol for

several times and then dried in vacuum. Finally, the dried PNIPAAm-g-TiO₂ powders were preserved in a desiccator before use. The schematic diagram of thermo-responsive behavior of a nanoparticle is shown in Fig. 1.



Scheme 1 The schematic representation of two-step synthesis of nanoparticles

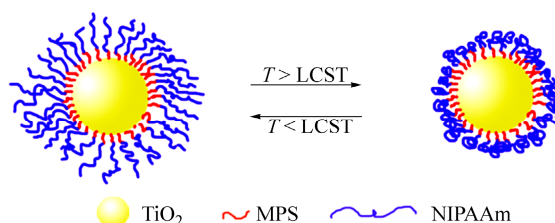


Fig. 1 Schematic diagram of thermo-responsive behavior of a TiO₂-g-PNIPAAm nanoparticle

Preparation of PVDF/TiO₂-g-PNIPAAm Nanocomposite Membranes

All the membranes were prepared by classical phase inversion method with PVDF as bulk material, DMAc as the solvent, TiO₂-g-PNIPAAm as the additive, and PVP as the pore-forming agent according to the compositions listed in Table 1. TiO₂-g-PNIPAAm particles (0 wt%, 1 wt%, 2 wt%, 3 wt%, and 4 wt% based on the weight of PVDF) and DMAc solvent were first imported into a round-bottom flask and then PVDF powders were added after the suspension was under ultrasonic dispersion for 2 h. The casting solution was then mechanically stirred at 70 °C for at least 24 h until the nanoparticles were downright dispersed. After fully degassing, the casting solution was spread onto clean glass plates with 200 μm gap which were then immersed into a coagulation bath (distilled water) for 1 min. After peeling off from the glass plates, the resultant membranes were rinsed in distilled water for 48 h to remove residual solvent and dried at room temperature. The nanocomposite membranes were denoted as M0, M1, M2, M3, and M4 according to the weight percentage of TiO₂-g-PNIPAAm.

Table 1. Composition of casting solution for membranes

Membranes	TiO ₂ -NIPAAm (wt%)	PVDF (wt%)	PVP (wt%)	DMAc (wt%)
M0	0	14	3	83
M1	1	13	3	83
M2	2	12	3	83
M3	3	11	3	83
M4	4	10	3	83

Nanoparticle and Membrane Characterization

Surface chemical composition of nanoparticles and membranes

The chemical composition of nanoparticle was analyzed by FTIR spectroscopy (Thermo Nicolet 360, Nicolet, USA). The graft degree of polymer was tested *via* TGA (NETZSCH, Germany) from 20 °C to 900 °C under N₂ atmosphere. The size and microstructure of nanoparticles were determined by a JEOL transmission electron microscope (TEM, JEOL JEM-200CX) at 120 kv. The chemical composition of membrane surface was investigated by ATR-FTIR and XPS (PHI 5000C ESCA system, PHICo., USA).

Porosity and mean pore radius of membranes

The porosity of membranes was determined by the dry-wet membrane method. The membrane in water was weighed after mopping superficial water with filter paper. Then the dry weight was measured after the wet membrane was dried in air. The porosity ε was calculated as^[18],

$$\varepsilon (\%) = (W_w - W_d) / \rho A l \times 100 \quad (1)$$

where W_w denotes the weight of wet membrane and the W_d is weight of dry membrane. ρ is the water density (0.998 g/cm), l is the membrane thickness (m) and A is the area of the membrane (m²).

The mean pore radius (r_m) was determined by filtration velocity method, according to Guerout-Elford-Ferry equation^[18],

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q}{\varepsilon A \Delta P}} \quad (2)$$

where η is water viscosity (8.9×10^{-4} Pa·s), l is the membrane thickness (m), ΔP is the operation pressure (0.1 MPa), ε is the porosity of the membrane (%), Q is volume of permeate water per unit time (L/s).

Surface morphology

The surface morphology and the cross-section of membranes were observed by scanning electronic microscopy (FESEM, SIRION-100, FEI Co. Ltd.). To study the cross-section of the membranes, the membranes were fractured in liquid nitrogen. The membrane samples for SEM analysis were initially dried in nitrogen gas, and then were sputter-coated with gold-palladium alloy to a thickness of 5 nm before microscopic analysis.

Surface of thermo-responsive membranes

The static contact angle of water droplets on the membrane surface was measured *via* the sessile drop method using the OCA 20 contact angle system (Dataphysics Instruments with GmbH, Germany). Test conditions: temperature 20–40 °C, relative air humidity 46%, droplet size 1 μ L. In order to minimize experimental error, the contact angles were measured five times for each sample and then were averaged.

Static protein adsorption of thermo-responsive membranes

The nanocomposite membrane was washed with phosphate buffer for 24 h to remove the active groups and pollutants on membrane surface. The sample was immersed into six test tubes with BSA solution (1 g/L) and then shaking for 24 h under 23 °C and 37 °C (M0–M4). Until adsorption equilibrium, the membrane was removed and rinsed with 5 mL phosphate buffer solution, which was added into the stoste, then the absorbance of BSA solution was measured ($\lambda = 280$ nm) for concentration determination. The BSA adsorption capacity of the membrane was calculated according to the concentration change of the BSA solution.

Filtration experiments

The filtration experiments were performed using a 60 mm diameter thermostated dead ended stirred filtration cell (0.1 MPa, 25 ± 0.1 °C). The flux of pure water (J_w) was obtained from the volume of the permeated water within 30 min and calculated as:

$$J = V / A \times \Delta t \quad (3)$$

where J is the pure water and BSA flux (L/m²h), V is the permeate volume (L), A is the membrane area (m²) and Δt is the time (h). After that, 1 g/L BSA (PH = 7.4) phosphate-buffered saline solution was forced to permeate through membrane at the same pressure for 60 min and the flux was recorded as J_p . After filtration of BSA solution, these membranes were cleaned *via* shaking in pure water for 2 h at 25 °C and then the pure water fluxes (J_R) were measured again. By comparing the value of J_w , J_p and J_R , the water flux recovery and the cleaning property of the fouled membrane were investigated. The flux recovery ratio (FRR) was calculated as follows:

$$\text{FRR} (\%) = (J_{w2} / J_{w1}) \times 100\% \quad (4)$$

The BSA rejection ratio (R) was calculated by the following equation:

$$R (\%) = (1 - C_p / C_f) \times 100 \quad (5)$$

where C_p and C_f (g/L) represents the concentrations of permeate and feed solution, respectively.

Stability of nanocomposite membranes

The hydrophilic stability of nanocomposite membranes was investigated *via* measuring the water contact angle on membrane surface. Each grafted membrane specimen was immersed in water and leached by continuous shaking for various time at 20 °C. Each time after drying the leached membranes, the water contact angle was measured again and used as the stability indicator of membrane hydrophilicity.

The retention ratio tests of nanoparticles were performed using the dead ended stirred filtration cell for 20 days (0.2 MPa, 20 °C). The membrane was dried naturally after water flux testing every 4 days, and then weighed and tested the contact angle. The stability of nanoparticles in membranes can be expressed as

$$RM (\%) = W_i / W_0 \times 100 \quad (6)$$

where W_0 (g) and W_i (g) are the initial mass and the i th residual mass of membranes.

Mechanical properties of membranes

Mechanical properties including tensile strength and percentage of elongation at break were measured with a Texture Analyzer (Stable Micro System TA. XT-plus, UK) following the ASTM Standard Test Method D882-91 (ASTM, 2003). The samples were mounted between the grips with an initial separation of 5.0 cm, and the cross-head speed was set at 1.0 mm/s.

RESULTS AND DISCUSSION

TiO₂ Nanoparticles Modification

FTIR spectra of nanoparticles

The modification of TiO₂ nanoparticles was investigated by FTIR, and the results are shown in Fig. 2(a). In the spectrum of pristine TiO₂ the sharp band at about 1650 cm⁻¹ and the broad band at around 3400 cm⁻¹ are due to adsorbed water on TiO₂ surface^[19–22]. The three new peaks appeared at 1704 cm⁻¹, 1639 cm⁻¹ and 1147 cm⁻¹,

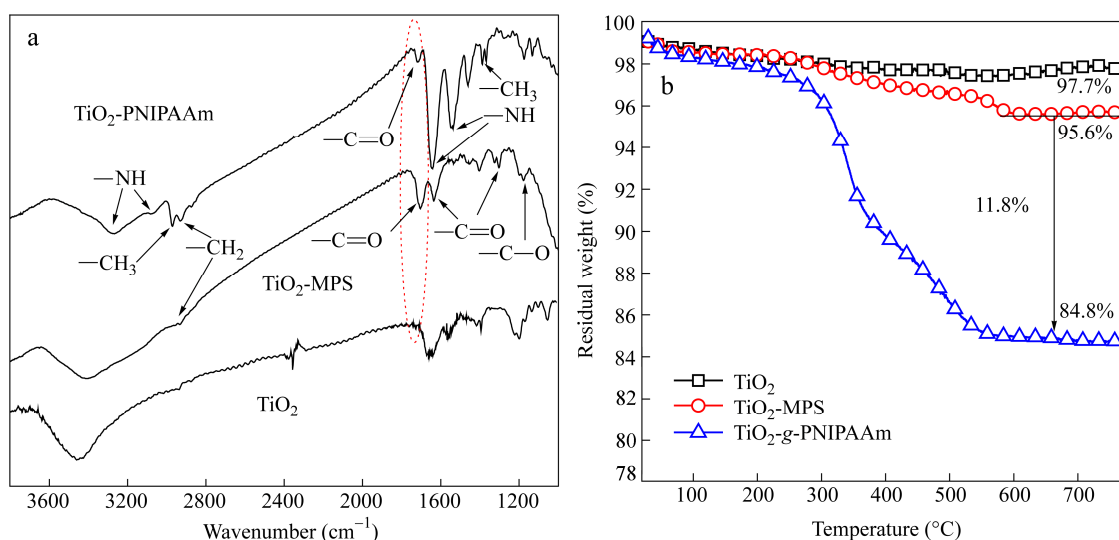


Fig. 2 (a) FTIR spectra of TiO₂-g-PNIPAAm nanoparticles and (b) TGA curves of TiO₂, TiO₂-MPS and TiO₂-g-PNIPAAm nanoparticles

corresponding to the C=O, C=C and C—O stretching vibrations, respectively. The new peaks confirmed the well-done surface polymerization of MPS by “graft-from” polymerization. The C=C on TiO₂ surface acts as the active point for the further modification. The new characteristic absorption peaks of TiO₂-g-PNIPAAm at 1715 cm⁻¹ and 1644 cm⁻¹ were ascribed to C=O and N—H stretching vibrations of amide, respectively. Two new characteristic peaks at 2974 cm⁻¹ and 2915 cm⁻¹ were ascribed to methylene groups. These results confirmed the successful grafting of PNIPAAm on the TiO₂ surface.

TGA analysis of TiO₂-g-PNIPAAm nanoparticles

As shown in Fig. 2(b), TGA was conducted to investigate the graft degree of MPS and NIPAAm on nanoparticles. The graft degrees were 1.1% and 11.8% for MPS and NIPAAm from the TGA curves, respectively. The graft degree of MPS was low, because the dehydration reaction proceeded between the surface of TiO₂ and MPS monomer. Hence, the first step reaction provided a large number of double bonds on nanoparticles surface. The results further suggested the success of the “graft-from” polymerization for NIPAAm.

TEM characterization of TiO₂-g-PNIPAAm nanoparticles

In order to investigate the particle size and the microstructure of TiO₂ before and after the modification, the TEM observation of TiO₂, TiO₂-MPS and TiO₂-g-PNIPAAm nanoparticles was conducted, and the results are shown in Fig. 3. It can be seen that a polymer layer appeared on the nanoparticle surface after the reaction in Fig. 3(b) and 3(c). And in Fig. 3(c), the thicker polymer layer exhibited after the radical polymerization. The size of nanoparticles was about from 10 nm to 50 nm in TEM images. From the images, we can conclude that the MPS and PNIPAAm had been successfully grafted to the surface of TiO₂ nanoparticles.

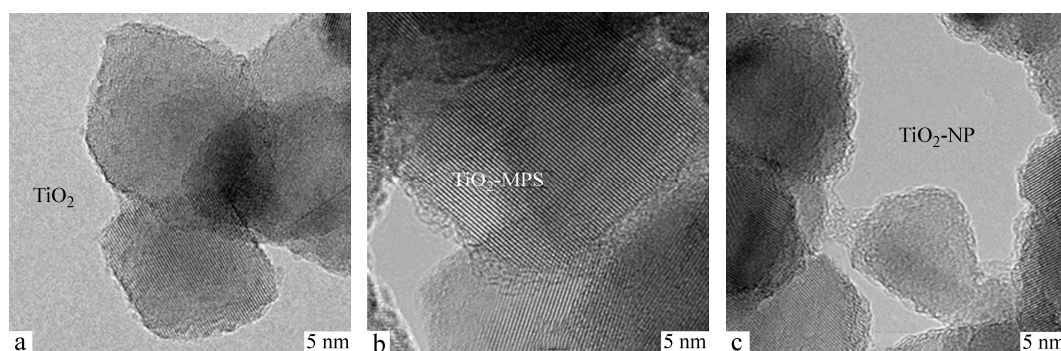


Fig. 3 TEM image of (a) TiO₂, (b) TiO₂-MPS and (c) TiO₂-g-PNIPAAm nanoparticles

Chemical Compositions of Nanocomposite Membranes

ATR-FTIR characterization of nanocomposite membranes

The functional group changes of membrane surface was investigated *via* ATR-FTIR, and the results are shown in Fig. 4. Compared with PVDF membrane (M0), in the spectra of PVDF/TiO₂-g-PNIPAAm nanocomposite membranes appeared two new peaks at 1680 cm⁻¹ and 1533 cm⁻¹, which suggested the vibrations of C=O and N—H groups, respectively. Moreover, the peak intensity of C=O groups in membrane enhanced around 1680 cm⁻¹. The results confirmed PVDF/TiO₂-g-PNIPAAm nanocomposite membranes could be facilely fabricated through addition of TiO₂-g-PNIPAAm nanoparticles in casting solutions before the wet phase inversion process.

XPS characterization of nanocomposite membranes

The chemical composition change of PVDF pristine membrane (M0) and the nanocomposite membrane (M4) was further analyzed by XPS, and the results are shown in Fig. 5(a). For M0, only C and F bands were observed in wide-scan spectrum (Fig. 5a), at 285.8 eV for C1s and 689.4 eV for F1s. As for M4, four new peaks were observed, 530.50 eV for O1s, 458.34 eV for Ti2p, 439.26 eV for N1s and 101.48 eV for Si2p, respectively. The

increasing intensity of N1s, O1s and Ti2p peaks with the dosage of modified TiO_2 suggested the increase of TiO_2 -g-PNIPAAm nanoparticles on the membrane surface.

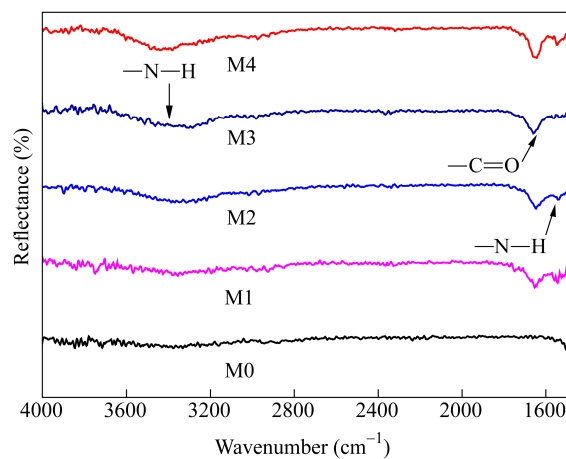


Fig. 4 FTIR-ATR spectra of PVDF/ TiO_2 -g-PNIPAAm nanocomposite membranes

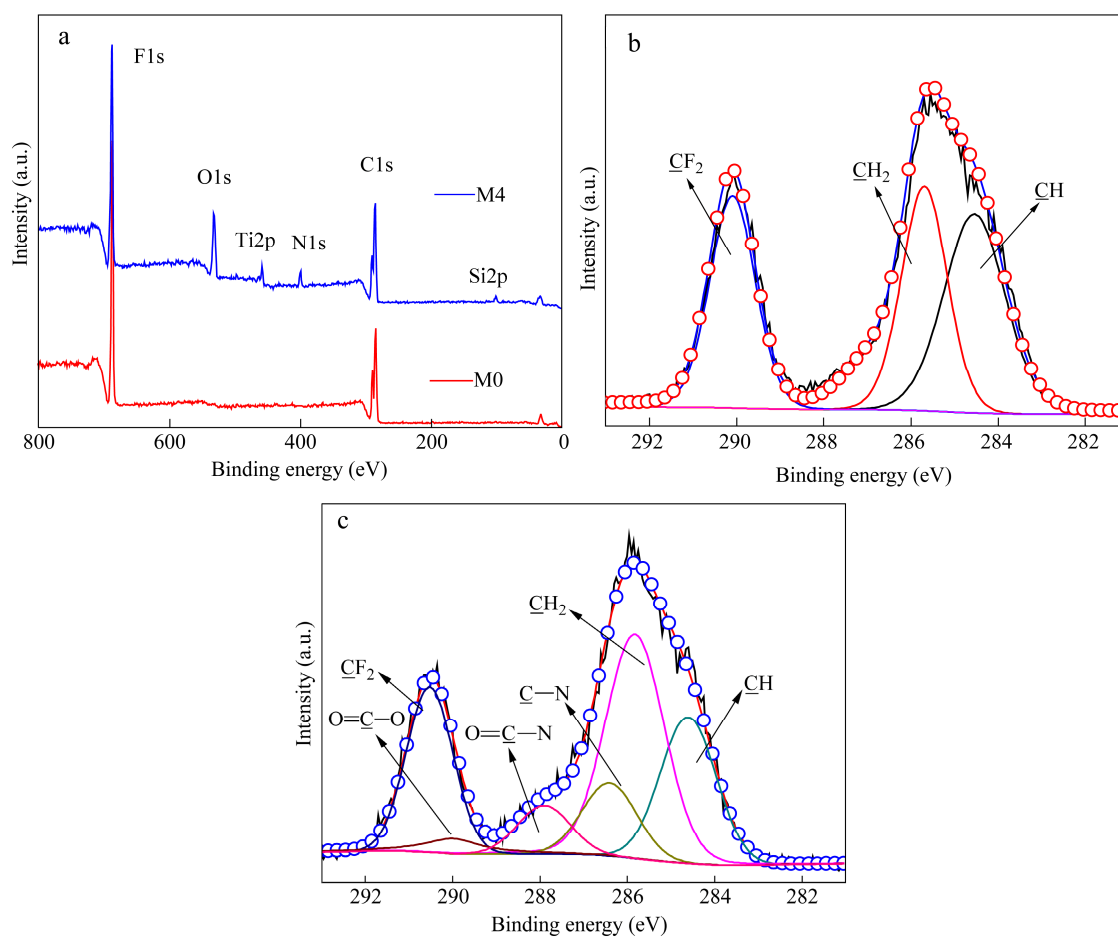


Fig. 5 XPS spectra of (a) M0 and M4, (b) C1s core-level XPS spectra of M0, (c) C1s core-level XPS spectra of M4

To further investigate chemical composition changes on membrane surface, the C1s spectra are divided into several peaks that represent different chemical environment of M0 and M4 (Figs. 5b and 5c). In case of M0, the C1s core-level spectrum can be divided into three peaks, with binding energies at 284.60 eV for the $-\text{CH}$ species, 285.82 eV for the CH_2 species (adjacent to the $-\text{CF}_2$ species in PVDF) and 290.52 eV for the $-\text{CF}_2$ ones. The $[-\text{CH}_2]:[-\text{CF}_2]$ peak area ratio of about 1:1 is consistent with the chemical structure of PVDF. For M4, the C1s core-level spectrum can be divided into six peaks. In addition to the peaks at 284.65 eV for the $-\text{CH}$, 285.80 eV for the $-\text{CH}_2$ (PVDF) and 290.5 eV for the $-\text{CF}_2$ observed for M0, three new peaks appear at 286.27 eV for the $-\text{C}-\text{N}$ species, 286.5 eV for $-\text{O}=\text{C}-\text{N}$ species and 288.8 for $-\text{O}=\text{C}-\text{O}$ species. The results demonstrated that the nanoparticles were migrated successfully to the membrane surface.

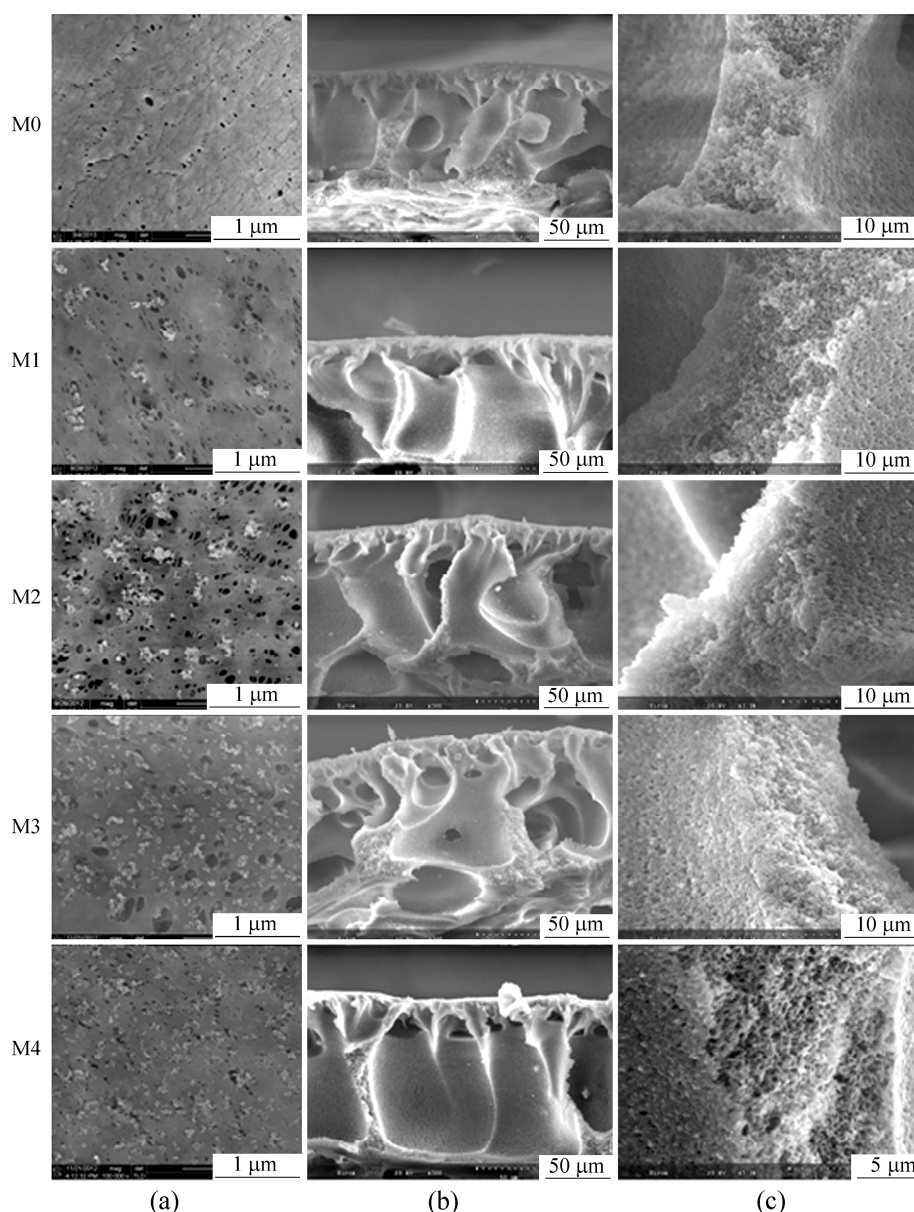


Fig. 6 SEM images of upper surface (a), cross-section (b) and (c) for prepared PVDF/TiO₂-g-PNIPAAm membranes M0, M1, M2, M3, and M4

Structure and Morphology Characterization of Nanocomposite Membranes

The surface and cross-section morphology of the pristine membrane (M0) and nanocomposite membranes (M1–M4) were studied *via* SEM, and the results are given in Fig. 6. The surface segregation of TiO₂-g-PNIPAAm has a great impact on the morphology of the membrane surface as shown in Fig. 6(a). Compared with M0, the nanoparticles of M1–M4 were dispersed on the membrane surface. Moreover, the number of nanoparticles on surface of M1–M4 membranes increased obviously with the dosage increasing.

The pore size and pore density of M1–M4 are large and high compared to those of M0. And the pore size decrease of M4 is because of the high dosage of nanoparticles in casting solution. All the cross-sections of membranes show the finger-like pore structure. The images (Fig. 6c) of randomly selected portions of the cross-sections, indicate the nanoparticles are evenly dispersed in membranes M1–M4.

It is observed that the nanocomposite membranes have a homogeneous surface and cross-section, which is very important to membrane filtration process. The homogeneous surface and cross-section are attributed to the good compatibility between PVDF and TiO₂-PNIPAAm. This good interaction is thought to be helpful for stabilization of TiO₂-PNIPAAm in PVDF in a rational way.

To further investigate the impact of membrane structure on permeability, the porosity and mean pore size are described in Fig. 7. The porosity and mean pore size increased with the increasing amount of nanoparticles in casting solutions. For M2, the porosity and mean pore size acquired the maximum at 2% of nanoparticles. The trend also can be clearly observed in SEM images (Fig. 6). The results demonstrated that the porosity and mean pore size can be controlled by adding different dosage of nanoparticles.

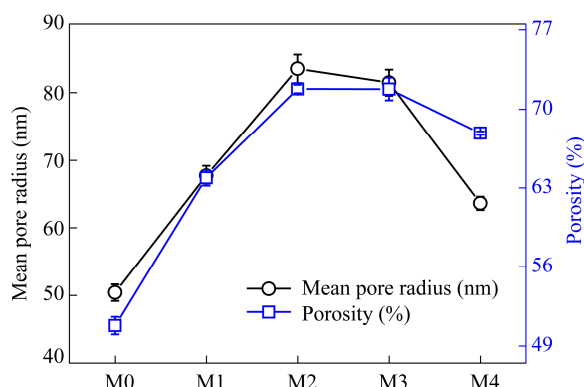


Fig. 7 Porosity and mean pore radius of membranes (M0, M1, M2, M3 and M4)

The Thermo-responsive Performance of PVDF/ TiO₂-g-PNIPAAm Membranes

Contact angle of thermo-responsive nanocomposite membranes

To investigate the thermo-responsive PVDF/TiO₂-g-PNIPAAm nanocomposite membrane, the contact angle was measured from 20 °C to 40 °C (Fig. 8). The contact angle of M1–M4 were all smaller than that of M0, which indicated the TiO₂-g-PNIPAAm nanoparticles could increase the hydrophilicity of PVDF membranes below or above the LCST. The contact angle of nanocomposite membranes decreased with the increasing dosage of nanoparticles below the LCST. However, the contact angle became larger with increasing nanoparticles above the LCST, and these values were 83.67, 76.62, 79.92 and 78.41° for M1, M2, M3 and M4 at 40 °C, respectively. A certain amount of hydrophilic —NH groups of the PNIPAAm on swollen state ($T < \text{LCST}$) led to the contact angles becoming smaller from M1 to M4. Conversely, the hydrophobic PNIPAAm chain segments on shrinkage state ($T > \text{LCST}$) result in the contact angles increasing. Therefore, the contact angles of nanocomposite membranes exhibited a big change near the LCST.

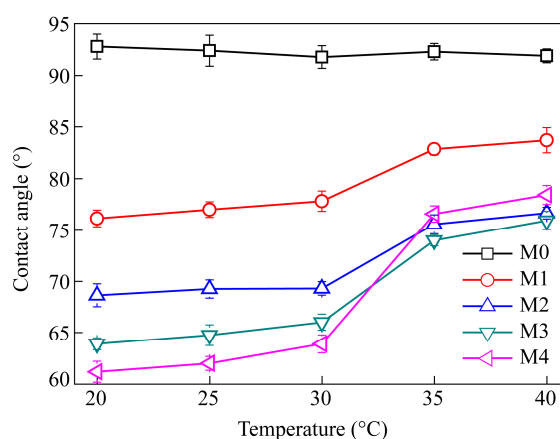


Fig. 8 The contact angles change of membranes under different temperatures

BSA static adsorption of nanocomposite membranes

Bovine serum albumin (BSA) is usually used to evaluate the antifouling ability of separation membranes^[23]. This study selected five samples including pristine PVDF membrane and nanocomposite membranes. It can be seen from Fig. 9, the BSA adsorption of nanocomposition membranes was much lower than that of the pristine PVDF, and the difference became increasingly apparent with the increase of nanoparticles at 23 °C. And the BSA adsorption became higher at 40 °C than that at 23 °C. These results suggested that the nanocomposite membranes obtained a good hydrophilicity, and their antifouling performance also enhanced as the nanoparticles existed on the membrane surface. The hydrogen bonds formed between the hydrophilic groups ($-\text{CONH}$) and water molecules below the LCST. And the combined effect of these hydrogen bonds in the periphery of the PNIPAAm chain can form a stable hydrophilic shell, resulting in a wider range of lower BSA adsorption. On the contrary, the contracted brushes formed a hydrophobic layer that enhanced the BSA adsorption on membrane surface above the LCST^[24].

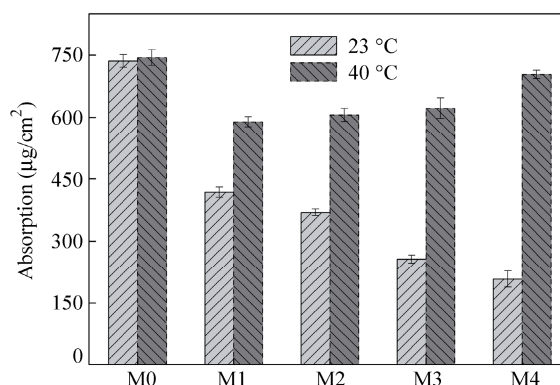


Fig. 9 Amount of BSA adsorbed per unit area of membranes

Water flux of nanocomposite membranes

The relationship between the water flux of the membranes and the temperature was investigated (Fig. 10). In the range of measured temperatures, the water flux of nanocomposite membranes was larger than that of the pristine membrane because the PVDF/TiO₂-g-PNIPAAm membranes possessed higher pore density and pore diameter (Fig. 4). And the water flux increased greatly with temperature above the LCST. However, nanocomposite membrane M2 acquired the biggest water flux that reached 212.1 L/m²h at 40 °C, the value was almost 1.96 times to the flux at 23 °C. The flux of M4 was the lowest due to the smallest mean pore size and porosity. The results suggested that the flux of membranes was decided by two factors, LCST and pore parameters. The

changes of flux was because the hydrophilic/hydrophobic transition of PNIPAAm polymer brushes occurred around the LCST resulting in thermo-responsive “OFF”/“ON” performance of membrane pores^[25].

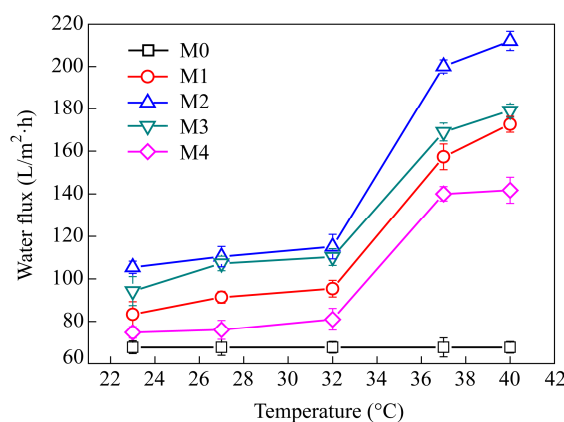


Fig. 10 Water flux of nanocomposite membranes under different temperatures

The membrane pores were in the “off” state under the LCST, resulting in the decline of water flux. In contrast, the brushes huddled together causing the “open” state of pores which led to the increased water flux^[26–28]. Based on the analysis above, the nanocomposite membranes obtained a good thermo-responsive ability.

Filtration experiments

To further investigate the fouling-resistance of membranes in detail, dynamic protein filtration was performed. The J_{w1} , J_p , J_{w2} and water recovery ratio of membranes are shown in Fig. 11. The changes of membrane flux were nearly identical to the trend in Fig. 10, which should be attributed to the thermo-responsive “OFF”/“ON” performance of membranes pores. The water flux recovery ratio (FRR) had a great increase with the growing dosage of nanoparticles at 23 °C. And the values were 47.1%, 85.1%, 88.4%, 91.4% and 92.3% for M0–M4, respectively. The improvement of FRR suggested the PVDF/TiO₂-g-PNIPAAm membranes can be cleaned easily by water. However, the FRR exhibited a slightly downward trend from M1 to M4 at 40 °C in Fig. 11(b) because the PNIPAAm brushes on the shrinkage state caused the easy adsorption of BSA.

And more protein was adsorbed on membrane surface and in membrane pores with increase the number of nanoparticles. This behavior led to the decline of pore size, and it was rather difficult to remove the adsorbed protein. Hydrophilic TiO₂ also had great contribution to reducing the protein fouling. The nanocomposite membranes possessed a good anti-pollution property by combining the hydrophilic TiO₂ with NIPAAm. The hydrophilic layer on the membrane surface can effectively reduce the adsorption of BSA.

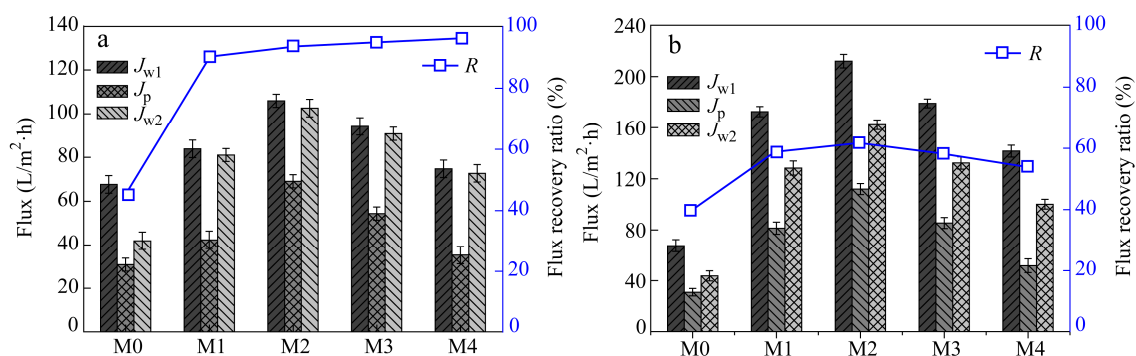


Fig. 11 Permeation fluxes of water and BSA solution, and the water recovery ratio of one cycle for the membranes at 23 °C (a) and 40 °C (b)

BSA rejection ratio of membranes

In the filtration experiments, the BSA rejection ratio of membranes was calculated (Fig. 12). It can be found that the rejection ratio of nanocomposite membranes obtained a great improvement compared to that of the PVDF membrane, and the effect at 20 °C was better than that at 40 °C. Moreover, the nanocomposite membranes exhibited an increasing BSA rejection ratio along with the increase of nanoparticles, and M4 acquired a maximum value (90.45%) due to the large number of hydrophilic nanoparticles and small pore size at 20 °C. Whereas, M2 acquired the highest BSA rejection ratio at 40 °C because of the nanoparticles on the hydrophobic state.

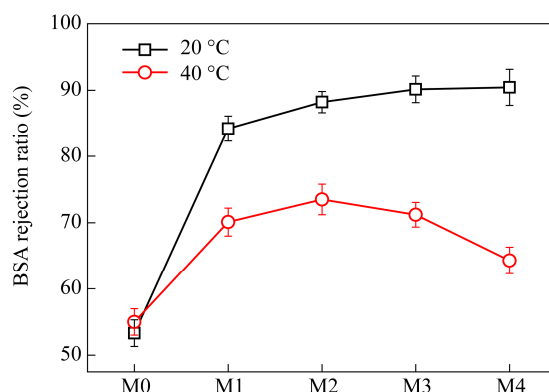


Fig. 12 BSA rejection ratio of membranes at 20 °C and 40 °C

Hydrophilic Stability of Nanocomposite Membranes

The contact angle was measured every 5 days to investigate the hydrophilic stability of nanocomposite membranes (Fig. 13a). The initial contact angle gradually increased in 10 days, and without further increasing after 15 days. The combination between PVDF and TiO₂-g-PNIPAAm was very stable for the interlacing between the PNIPAAm and the PVDF chains. That is to say, the nanocomposite membranes obtained hydrophilic stability.

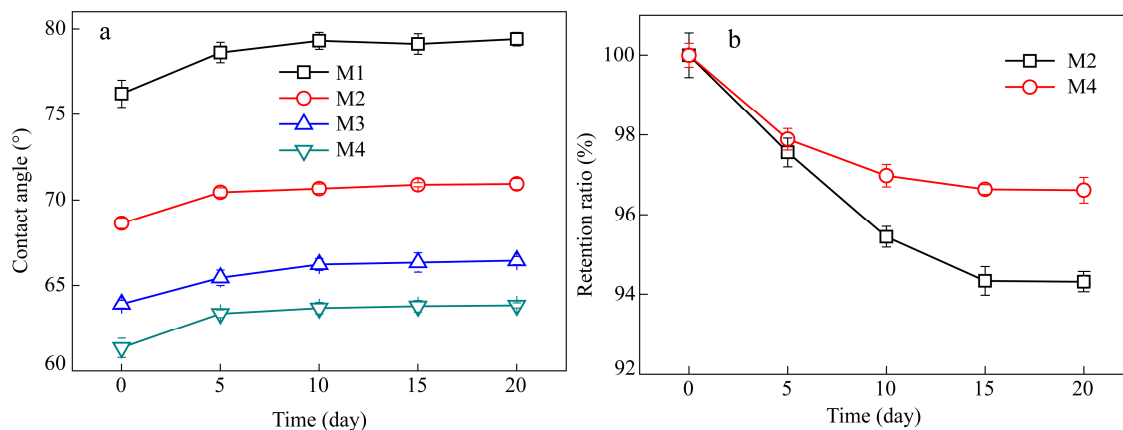


Fig. 13 (a) Time-dependent contact angle and (b) retention ratio of membranes

Retention Ratio of Nanocomposite Membranes

The retention ratio of nanocomposite membranes (M2 and M4) was measured, shown in Fig. 13(b). It can be found that the retention ratio of membranes gradually decreased, and without further change after 15 days. What's more, the retention ratio of M2 was higher than that of M4 as the high nanoparticles dosage in M4. The changes of retention ratio were determined directly by the leakage of nanoparticles in membranes. The results suggested that TiO₂-g-PNIPAAm was firmly bound in membranes.

Mechanical Properties

Tensile strength and elongation at break are two important parameters to describe the mechanical properties of membranes. The effect of TiO₂-g-PNIPAAm dosage on the mechanical strengths of the PVDF nanocomposite membranes is shown in Table 2. The tensile strength and elongation at break first increased with the increase of nanoparticle dosage, and attained their peaks of 5.35 MPa and 29.83% for M2 and M3, respectively, then decreased. Certain amount of nanoparticle dosage suppressed the formation of macrovoids and improved the mechanical properties of nanocomposite membranes. More nanoparticle dosage made the membrane more rigid and weakened the mechanical properties of PVDF hybrid membranes. Whereas, all the tensile strength and elongation at break of nanocomposite membranes were high than those of the PVDF membrane, because the PNIPAAm brushes on TiO₂ surface enhanced the affinity between PVDF and modified nanoparticles^[29].

Table 2. Mechanical properties of the fabricated PVDF/PVP-g-MMT nanocomposite membranes M0, M1, M2, M3 and M4

Membrane	Tensile strength (MPa)	Elongation at break (%)
M0	4.30 ± 0.23	17.21 ± 0.34
M1	4.94 ± 0.31	23.43 ± 0.25
M2	5.35 ± 0.19	27.12 ± 0.42
M3	4.88 ± 0.26	29.83 ± 0.27
M4	4.41 ± 0.41	20.52 ± 0.37

CONCLUSIONS

In summary, a facile approach for synthesizing hydrophilic and functionalized nanocomposite additive, TiO₂-g-PNIPAAm, was developed to fabricate PVDF/TiO₂-g-PNIPAAm nanocomposite membranes for water treatment. As a surface hydrophilic additive, TiO₂-g-PNIPAAm can easily migrate to membrane surface *via* segregation. As a self-dispersant, TiO₂-g-PNIPAAm could be well dispersed in the as-prepared PVDF/TiO₂-g-PNIPAAm nanocomposite membranes which can be attributed to the repulsion among TiO₂ particles with surface-grafted PNIPAAm in the casting solution. The contact angle measurements showed the modified membranes possessed enhanced hydrophilicity and obvious thermo-responsive properties. The well dispersion of TiO₂-g-PNIPAAm endowed nanocomposite membranes with better thermo-responsive flux, lower BSA adsorption, higher water recovery ratio and BSA rejection ratio compared with those of PVDF membranes. The mechanical strength of PVDF/TiO₂-g-PNIPAAm nanocomposite membrane was enhanced compared to PVDF membranes. These improvements should attributed to the functions of TiO₂-g-PNIPAAm in nanocomposite membranes, and the novel nanocomposite membranes have great potential for water treatment.

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