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One-step catechol-based biomimetic strategy to fabricate organic-inorganic hybrid coatings on PTFE flat membrane for the improvement of hydrophilicity and fouling resistance

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ABSTRACT

Recently, plant polyphenols had been proved to be potential candidates for dopamine because of their low-cost and similar coating ability. In this paper, a facile method was developed to modify the polytetrafluoroethylene (PTFE) flat microfiltration (MF) membrane via the co-deposition of catechol (CA) and silane coupling agent for the improvements of hydrophilicity and anti-fouling property. The membrane performance can be tuned by changing the concentration of silane coupling agent. After using this cheap and simple modification method, the PTFE flat membrane was endowed with excellent hydrophilicity, high water permeation flux and superior anti-fouling property. Moreover, interestingly, a colorless membrane was obtained by this method. Then, the anti-fouling test was conducted on the modified PTFE flat membranes. The as-prepared hydrophilic PTFE flat membranes possess excellent bovine serum albumin (BSA) fouling resistance. Finally, the surface stability of the modified membrane was studied and the modified membrane shows excellent stability under the acidic condition but weak to strong alkali.

Keywords: Polytetrafluoroethylene flat membrane; Catechol; Hydrophilicity; Fouling resistance

1. Introduction

Nowadays, there are still a lot of areas suffer from water shortages and water purification technology has been proved to be the most efficient approach to solve this problem [1–3]. Among these techniques, membrane separation has attracted much attention for its simple and cost-effective process [4–7]. The reason why the hydrophilic membrane was chosen as the basement membrane in membrane separation process is that the surface hydration can lead to a formation of a tightly bounded water layer upon the surface and prevent foulants from directly attached to the membranes [8,9]. PTFE flat membrane is a membrane material with suitable pore size, high porosity, high mechanical strength and good chemical stability and is a promising candidate for harsh water treatment [10]. However, the strong hydrophobicity of PTFE flat membrane causes a serious membrane fouling problem and limits its application in wastewater purification [11]. To improve membrane fouling resistance, hydrophilic modification of PTFE flat membrane is necessary.

On the past decades, much of efforts has been made to construct a hydrophilic layer on PTFE flat membrane. These methods, such as naphthalene sodium solution treatment [12,13], plasma treatment [14,15], surface grafting [16–18] and dip-coating [19,20] have been developed

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to solve this problem. Unfortunately, naphthalene sodium solution treatment destroys the surface of PTFE flat membrane which finally causes a decrease in membrane performance. The hydrophilicity of PTFE flat membrane treated by plasma usually decreases with time. The surface grafting is a relatively complex process and grafting uniformity is difficult to control. The most promising approach for practical application is dip-coating because of its simple operation process. Nevertheless, the stability of physical coating is dissatisfactory due to ultra low surface energy of PTFE flat membrane (γ =19.5 mN/m) [21]. Therefore, the development of a simple and effective method is urgent.

In recent years, mussel-inspired chemistry has been studied in detail to improve the hydrophilicity of the polymer membrane via a simple self-polymerization and deposition process of dopamine under the conditions of oxygen [22–25]. The results show that dopamine can form a firm coating on various substrates. The high price of dopamine, however, has been an obstacle to its practical applications. To solve this problem, Researchers were attempted to find a low-cost "dopamine". A vast number of polyphenols were proved to be potential candidates for dopamine because of their low-cost and similar coating ability [26–29].

Although polyphenols can form functionally versatile nano-coatings via dip-coating, the deposition process is time-consuming and the modified membrane shows poor hydrophilicity as well as anti-fouling property. It has been proved that co-deposition of polyphenols with other compounds is a facile strategy to accelerate reaction and improve hydrophilicity of polymer membrane simultaneously. Xu et al. [30] replaced dopamine with low-cost catechol and polyamine and fabricated hydrophilic polypropylene separator with excellent properties for Lithium-ion batteries. Wan et al. [31] co-deposited catechol with polyethyleneimine on polypropylene microfiltration membranes and the membranes with anionic dye solutions removal efficiency of over 99% are obtained. However, enhance the stability of coating on the surface of PTFE flat membrane by simply physical adsorption is not enough. In consideration of fiber network structure of PTFE flat membrane, construct a defect-free wrapping layer around every fiber is a feasible method. Because the mechanical interlocking between fibers and wrapping layers is beneficial to enhance the stability of wrapping layers.

Thus, compared with low molecular weight compounds which incline to form aggregates or particles, KH560 and KH590 are much easier to construct a defect-free wrapping layer or a film with polyphenols because these compounds are likely to form long-chain molecules via hydrolysis/condensation process [32–34]. In previous study, the PTFE flat membrane with excellent hydrophilicity and anti-fouling property was developed by co-deposition of CA/PEI and surface mineralization of KH560 via covalent bond [35], however, two-step reaction is not easy to operate. Therefore, further research is needed.

In this study, a one-step catechol-based biomimetic method was reported to fabricate organic-inorganic hybrid coatings on the PTFE flat membranes via co-deposition of CA and silane coupling agent. PTFE flat membranes with excellent hydrophilicity and water permeability were obtained, the coatings show excellent stability under strong acidic, neutral and weak alkaline environments. Besides, the modified membranes show superior stability in pure water filtration process. To the best of our knowledge, the substrates modified by CA/polyamine or dopamine/polyethyleneimine always show brown color which limits the applications of these methods [24,30,36]. This study also provides new insights into fabricating colorless coatings. Finally, the anti-fouling property and surface stability tests of modified membrane were conducted.

2. Materials and methods

2.1. Materials

Polytetrafluoroethylene flat membrane (mean pore size 0.22 μm, porosity 85%) was a commercial product supplied by Zhejiang Kertice Hi-tech Fluor-material Co., Ltd. Catechol (CA), tris-(hydroxymethyl)-aminomethane (Tris), Bovineserum albumin (BSA, Mn = 68000), tetraethyl orthosilicate (TEOS), (2,3-epoxypropoxy) propytrimethoxysilane (KH560) and (3-Mercaptopropyl) trimethoxysilanewere (KH590) were purchased from Aladdin (China). The phosphate-buffered saline (PBS, 0.1 M, pH = 7.4) was prepared by addition of prepackaged buffer salts (Aldrich) to deionized water. Other reagents such as ethanol, acetone and hydrochloric acid were provided by Hangzhou Gaojing Fine Chemical Industry Co., Ltd and used as received. All PTFE flat membrane samples were washed by acetone before used.

2.2. Modification of the PTFE flat membrane

CA and silane coupling agents were dissolved in a tris-buffer solution (pH = 8.5, 10 mM) with a designated mass ratio. The concentration of CA was 0.8 g/L for the following experiments. The PTFE flat membrane samples were immersed in the freshly prepared solution after pre-wetting with ethanol, and shaken at 25°C for 6 h. Then, the membranes were washed three times by deionized water to wash out the redundant CA/KH560 or CA/KH590 co-deposition particles and dried in a vacuum chamber at 40°C. The CA/KH560 or CA/KH590 modified membranes were obtained. In addition, TEOS was used to replace KH560 or KH590 for experiments and investigate whether the simply co-deposition of CA and TEOS by physical interaction is possible.

2.3. Characterization and instruments

Surface morphology of the PTFE flat membranes was observed by field emission scanning electron microscopy (FESEM, EVO MA 25, ZEISS). The PTFE flat membranes were sputtered with gold for 40 s. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Shimadzu AXIS Ultra DLD spectrometer (Kratos, XSAM800), using an Al Ka X-ray source. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were collected using a FTIR (Nicolet 5700, America) spectrophotometer. The contact angles of the membranes were measured by a contact angle measuring system (SL 200KB, America). The concentration of BSA solution was examined by UV-Vis spectrometer (Lambda 900, America) at 280 nm.

2.4. Tests of pure water flux and anti-fouling property

Pure water flux of the PTFE flat membranes was detected by a homemade dead-end filtration system (Fig. 1). The PTFE flat membranes were compacted at 0.2 MPa for 30 min to reach a stable value, and then the water flux was measured at 0.1 MPa. For the anti-fouling tests of the modified PTFE flat membranes, the treated membrane was immersed into 100 mL BSA solution (0.2 g/L, pH = 7.4) and shaken at 25°C for 24 h. The amount of adsorbed BSA was calculated from the different concentration of BSA in solution before and after BSA adsorption.

3. Results and discussion

3.1. Surface morphologies and chemical composition of the modified membranes

It is known that CA can be oxidized to a quinoid form and then deposit onto the surface of the membrane via self-polymerization in an alkaline Tris-buffer solution. The possible co-deposition pathway of CA with other compounds is shown in Fig. 2. For the co-deposition process of CA/KH560, hydrolysis/condensation of KH560 and crosslinking between CA and KH560 may be happened simultaneously. The phenolic hydroxyl groups derive from CA are easy to react with epoxy groups that derive from KH560 under the alkaline condition and then the defect-free wrapping layers are formed around every fiber of PTFE flat membrane [37,38]. Similar to the coating process of CA/KH560, the CA/KH590 networks can also form through Michael addition reaction between CA and thiol groups [39–42]. For the co-deposition process of CA/TEOS, the CA and TEOS are unable to coat the membrane well. The corresponding water contact angle (WCA) of CA/TEOS modified PTFE flat membrane is shown in below.

FESEM was employed to characterize the surface morphology of the PTFE flat membranes (Fig. 3). The insets of Fig. 3 are digital photos of different PTFE flat membranes. The white pristine PTFE flat membrane turns brown after modified by the CA/KH560 and the color is uniform, indicating a homogeneous modification. However, the CA/KH590 modified PTFE flat membrane is still colorless. Because the number of o-benzoquinone has created for CA self-polymerization, and the o-benzoquinone is brown. When CA and KH560 react, the o-benzoquinone was not broken, so the modified membranes of CA/KH560 are brown. While in the reaction of CA and KH590, the o-benzoquinone was broken, leading to a colorless membrane.

The pristine PTFE flat membrane (Figs. 3a,b) shows fiber network structure. After modified by the CA/KH560 (Fig. 3c,3d) or CA/KH590 (Figs. 3e,f), the fibers and nodes of PTFE flat membrane are wrapped by a thin film which is beneficial to enhance the fastness of the hydrophilic layer through mechanical interlocking since the interactions between hydrophilic layer and membrane are not strong enough. Moreover, the hydrophilic layer of the membrane is uniform and there is no obvious pore blockage happened on the membrane surface. These results indicate that negligible flux decrease can be achieved by this method.

The chemical composition of the membrane surfaces was revealed by XPS spectroscopy. As shown in Fig. 4, the pristine membrane only displays peaks of C 1s and F 1s at 284.75 eV and 689.29 eV, respectively. The new peaks of Si 2s and Si 2p arise after co-deposition of CA and KH560. The Si element is derived from hydrolysis product of KH560. As for the CA/KH590 modified membrane, besides Si 2s and Si 2p, the new peaks of S2s and S2p are observed which are

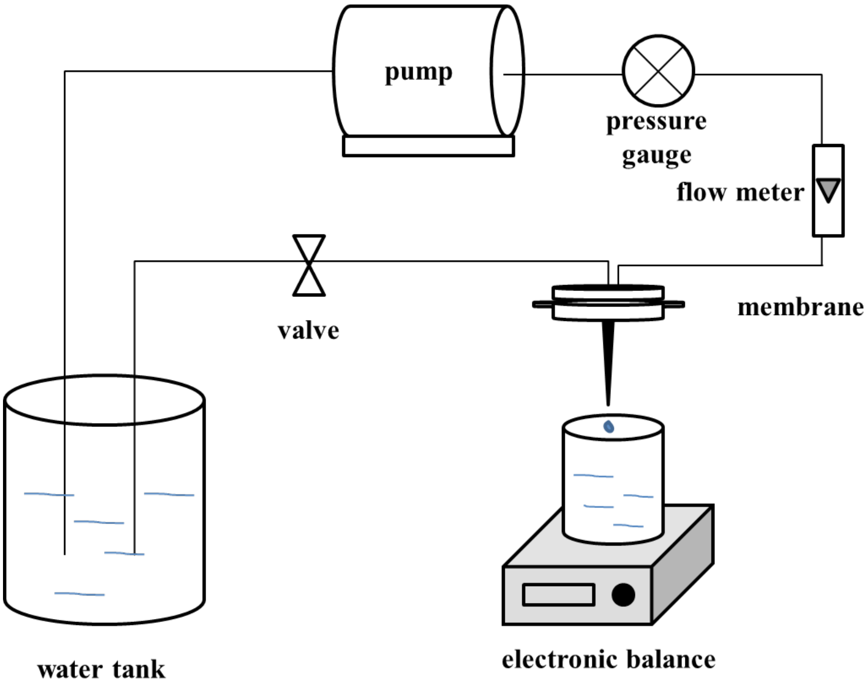

Fig .1. The homemade dead-end filtration system.

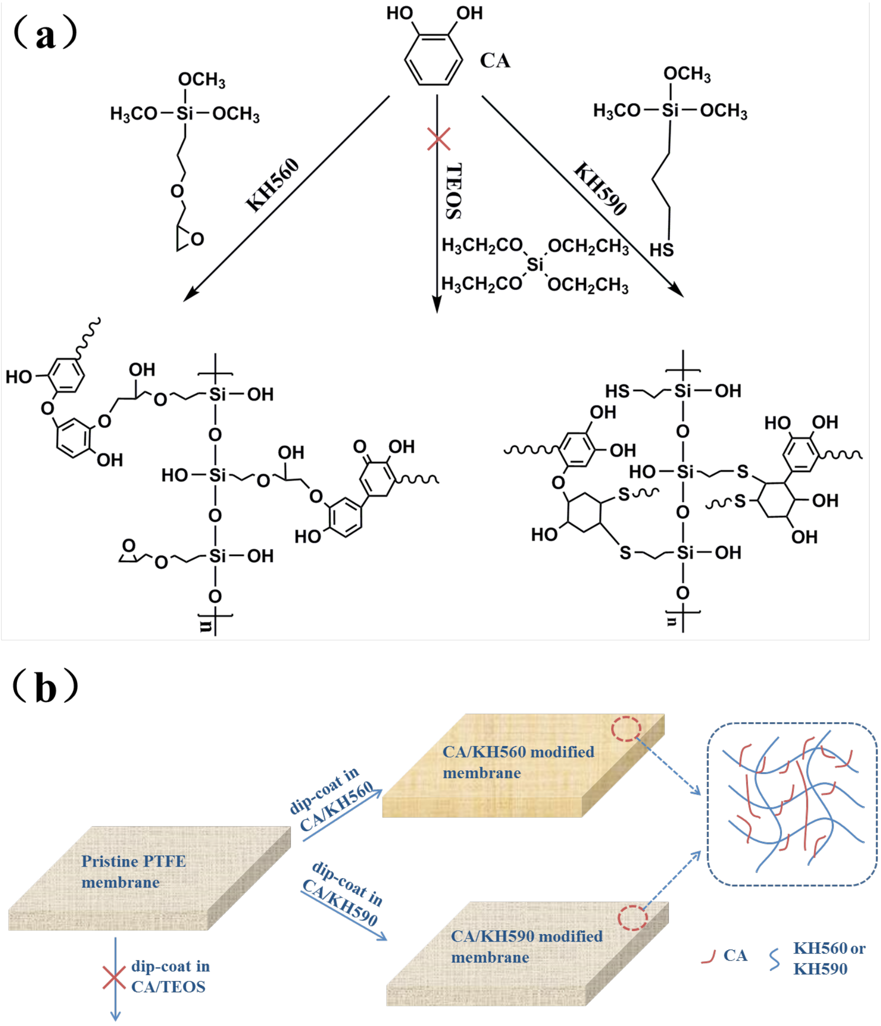

Fig. 2. (a) Possible chemical reaction mechanism between CA and silane coupling agents. (b) Schematic illustration for one-step fabrication of organic-inorganic hybrid coatings on PTFE membranes.

derived from hydrolysis product of KH590. These results suggest that the PTFE flat membranes are coated by CA/KH560 or CA/KH590 successfully. Finally, the elemental compositions of different PTFE flat membranes are shown in Table 1. The results are consistent with the XPS spectra well.

ATR-FTIR spectroscopy of the CA/KH560 and CA/KH590 modified PTFE flat membranes surface are shown in Fig. 5. Both of the modified membranes present the absorption peaks at 1038 cm^{-1} which is assigned to Si-O-Si stretch vibration derive from a silane coupling agent. For the CA/KH560 modified membrane, the new absorption band at 1500 cm^{-1} and 1560 cm^{-1} is attributed to C=C stretch vibration of the aromatic ring. Besides, the C-O-C stretch vibration at 1062 cm^{-1} suggests the successful reaction between CA and KH560. These results indicate that the PTFE flat membrane is successfully decorated by CA and KH560 via self-polymerization and crosslink. For the CA/KH590 modified membrane, the existence of C-S-C stretch vibrational 887 cm^{-1} is a strong evidence of the reaction between CA and KH590 through Michael addition reaction. Compared with the CA/KH560 modified membrane, there are no peak of aromatic ring appear in ATR-FTIR spectroscopy of the CA/KH590 modified membrane which indicates that the Michael addition reaction between KH590 and CA destroys π-π conjugation structure of the aromatic ring derived from CA. Moreover, appearance of $-CH_2$ absorption band at 2930 cm^{-1} also supports the above addition reaction. Therefore, the colorless phenomenon has been proved rational by these results. In addition, oxidation resistance of KH590 maybe another reason for this colorless phenomenon since the color is appearing only after the oxidation of CA.

3.2. Surface wettability and water permeability of the modified membranes

The wettability of various PTFE flat membranes was evaluated by static water contact angle (WCA) test (Fig. 6a). The pristine membrane shows a WCA of 145.2°±1.6°. After modified by CA/TEOS, the WCA of membrane declines to 124.5°±1.8° and the membrane still show hydrophobicity.

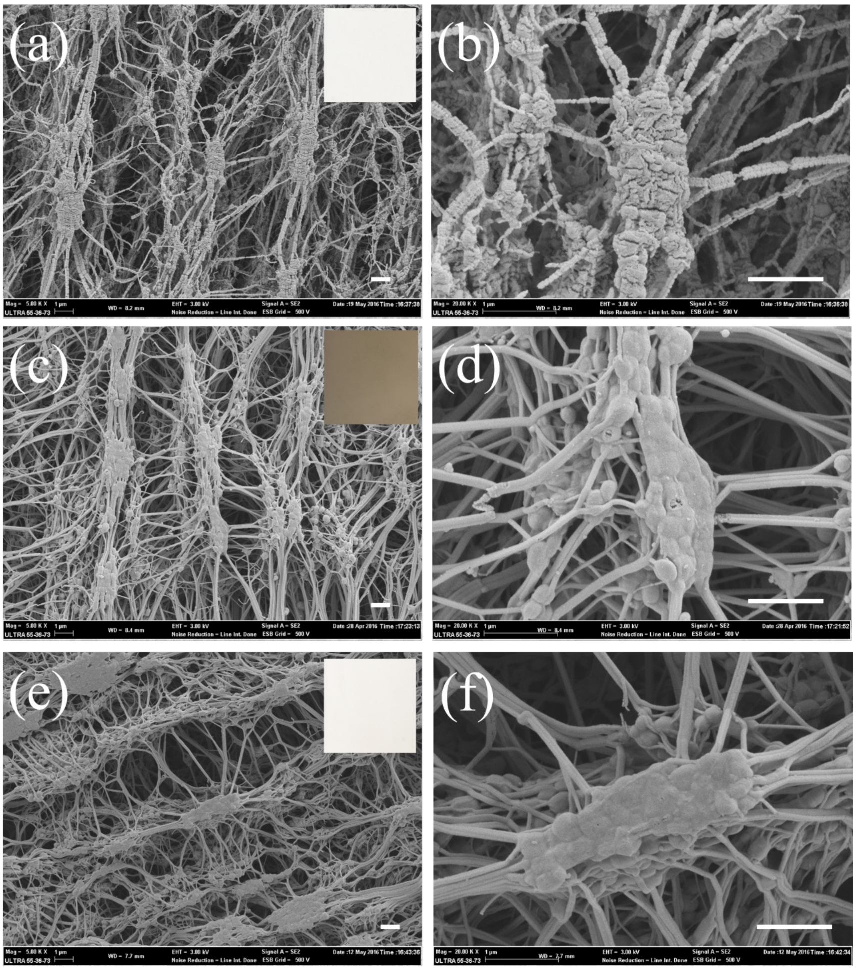

Fig. 3. SEM images of (a,b) the pristine PTFE membrane, (c,d) the CA/KH560 modified PTFE membranes with co-deposition times of 6 h (the mass ratio of CA/KH560 is 2:5), (e,f) the CA/KH590 modified PTFE membranes with co-deposition times of 6 h (the mass ratio of CA/KH590 is 2:4)(The scale bar is 1 μm).

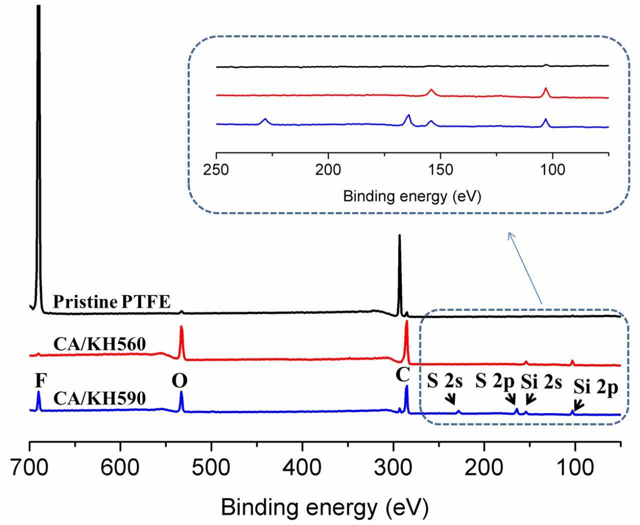

Fig. 4. XPS spectra of the pristine, CA/KH560 modified and CA/KH590 modified PTFE membranes.

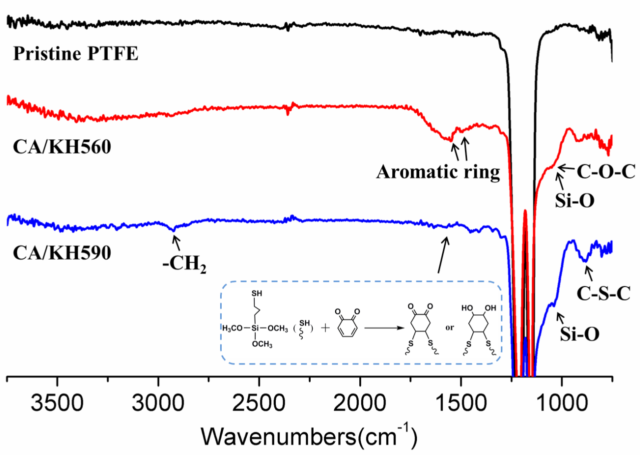

Fig. 5. ATR-FTIR spectra of the pristine, CA/KH560 modified and CA/KH590 modified PTFE membranes.

Table 1
Elemental composition of different PTFE flat membranes as determined by XPS

Membrane	Composition (At.%)				
	C	F	O	Si	S
Pristine PTFE	33.17	66.83	/	/	/
CA/KH560	71.37	2.13	21.9	4.6	/
CA/KH590	61.96	10.34	15.25	6.9	5.55

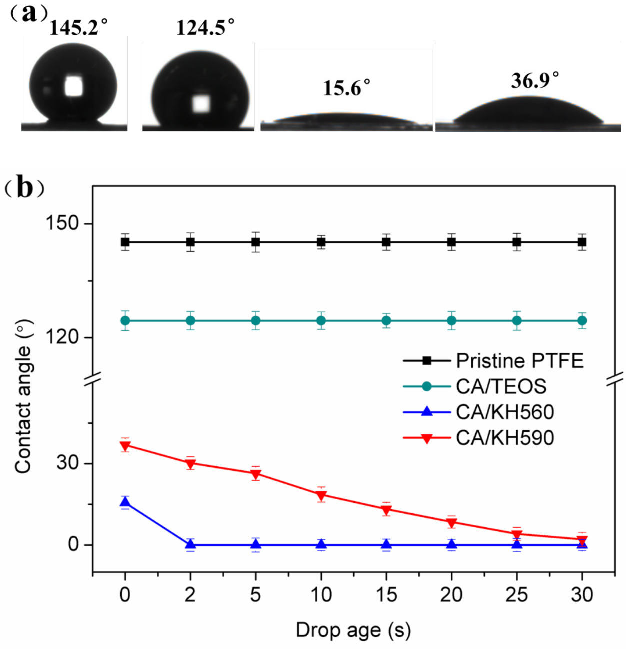

Fig. 6. (a) Images of water contact angle of the pristine, CA/TEOS modified, CA/KH560 modified and CA/KH590 modified PTFE membranes (from left to right). (b) Water contact angle of different membranes versus time.

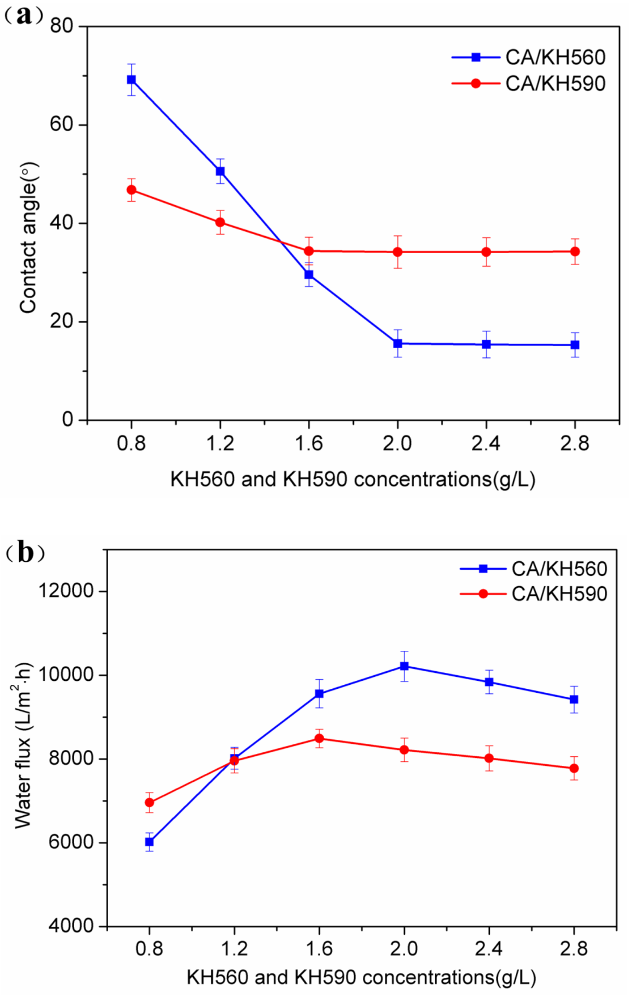

Fig. 7. The influences of KH560 and KH590 concentrations on (a) water contact angle and (b) water flux of the PTFE membrane.

The result indicates that the hydrophilic coatings are unable to form on the surface of PTFE flat membrane simply by physical interaction between CA and TEOS. The CA/KH560 and CA/KH590 modified membranes show a WCA of 15.6°±1.7° and 36.9°±1.2°, respectively. This low WCA is attributed to the hydrophilic nature of hydrolysis/condensation products of KH560 and KH590. Dynamic WCA test further demonstrates the effect of hybrid coatings on improving the wettability of the membranes (Fig. 6b). Both CA/KH560 and CA/KH590 modified membranes are completely wetted by droplet in 2 s and 30 s, respectively.

The water permeability of the modified PTFE flat membranes was evaluated by pure water flux test and the effect of KH560 or KH590 concentration on the WCA and water flux was investigated. As shown in Fig. 7a, the concentrations of KH560 and KH590 have an obvious effect on the WCA of PTFE flat membranes. Both the CA/KH560 and CA/KH590 modified membranes show a decrease in WCA with the increase of KH560 and KH590 concentrations. The best WCA are 15.6°±1.7° and 36.9°±1.2° for the CA/KH560 and CA/KH590 modified membranes, respectively. As the KH560 and KH590 concentrations increase further, the WCA tends to be stable. The effect of KH560 and KH590 concentrations on water flux is shown in Fig. 7b. The water flux of the CA/KH560 and CA/KH590 modified membranes were enhanced by the increase of KH560 and KH590 concentrations and reaches 10215±360 L·m^{-2}·h^{-1} and 8490±280 L·m^{-2}·h^{-1} when the corresponding concentrations are 2 g/L and 1.6 g/L, respectively. In contrast, the CA/KH590 shows larger coating rate but the CA/KH560 coatings are more hydrophilic. As the KH560 and KH590 concentrations increase further, the water flux begins to decrease due to the formation of thicker coatings on the fibers and nodes of PTFE flat membrane. These results indicate that more KH560 and KH590 are beneficial to accelerate crosslinking reaction and form coatings on the membrane. According to the above results, the mass ratios of 2:5 and 2:4 are the best reaction condition for the CA/KH560 and CA/KH590 modified membranes, respectively. Therefore, the following experiments were conducted on the pristine PTFE flat membranes under these mass ratios. The effect of co-deposition time on the mem-

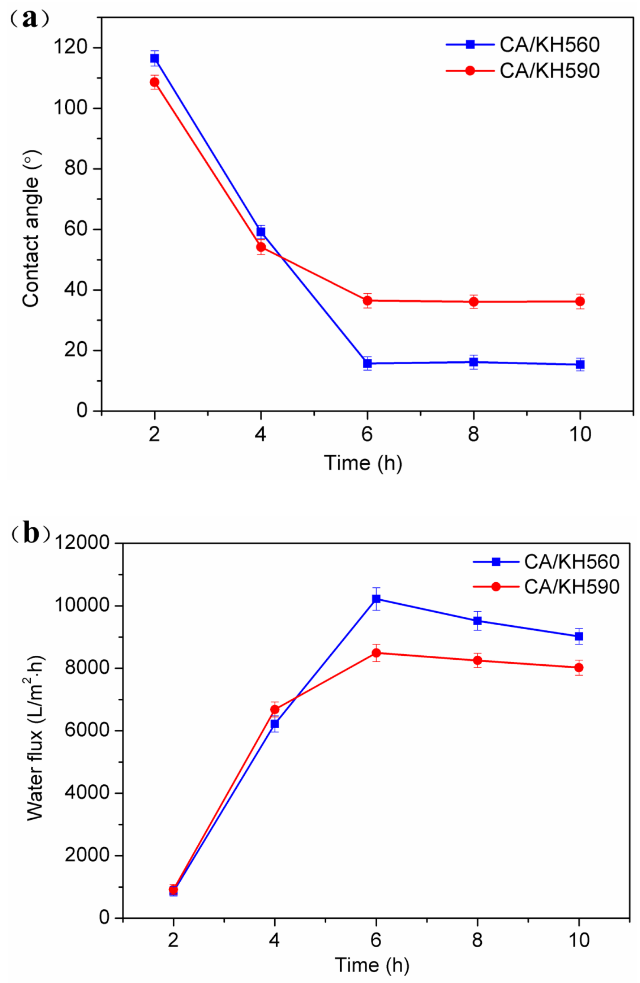

Fig. 8. The influences of reaction time on (a) water contact angle and (b) water flux of the PTFE membrane.

branes hydrophilization was also investigated. As shown in Fig. 8a, the WCA of the CA/KH560 and CA/KH590 modified membranes decreases with the increase of the co-deposition time. When the co-deposition time is more than 6 h, it begins to be stable. The water flux of the CA/KH560 and CA/KH590 modified membranes increases with the co-deposition time increase to 6 h (Fig. 8b). However, the water flux begins to decrease when co-deposition time is more than 6h which is ascribed to the formation of the aggregate particles and a slight pore blockage. Therefore, the best co-deposition time for these experiments is 6h. The membranes are used in following tests are fabricated under the best conditions.

3.3. Anti-fouling property of the modified membranes

Anti-fouling property is important for the membranes in long-term operation. Hydrophilic modification is an efficient approach to enhance the anti-fouling property of the membranes because the surface hydration can lead to the formation of a tightly bounded water layer upon the surface and prevent foulants from directly attached to the membranes. In addition, surface potential also plays an important role in the anti-fouling property of the membranes. Thus, Zeta potentials and BSA adsorption of the different PTFE flat membranes were measured at 25°C. Anti-fouling property test of the membrane has a variety of methods, such as continuous filtration of BSA [43], static adsorption of BSA [44]. In this study, anti-fouling property of membrane has been tested via static adsorption of BSA. As revealed by Fig. 9a, all of the membrane surfaces are negatively charged. The zeta potentials of the pristine membrane surface, CA/KH560 modified membrane surface and CA/KH590 membrane surface are –40.81±1.21mV, –46.8±0.91 mV and –70.68±1.04 mV when pH = 7.4, respectively. The BSA adsorption results are shown in Fig. 9b. The pristine PTFE flat membrane shows the highest adsorption of BSA due to the nature of the PTFE materials, indicating that the pristine membrane is easily fouled by protein in water. However, the CA/KH560 and CA/KH590 modified membranes show a decrease in BSA adsorption amount and the increase of KH560 and KH590 concentrations decrease the BSA adsorption amount further. Fig. 9c shows the results of static BSA adsorption on the membrane at different adsorption-cleaning time under pH = 7.4. It can be found that the adsorption of BSA of pristine membranes were decreased when a second and third time adsorption, but the adsorption of BSA of modified membranes almost unchanged. These results indicate that hydrophilic CA/KH560 and CA/KH590 coatings are crucial in improving the anti-fouling property of the membranes. In comparison, although the CA/KH560 modified membrane shows better hydrophilicity than the CA/KH590 modified membrane, the latter possesses better anti-fouling property for BSA. This result is attributed to stronger electronegativity of the CA/KH590 modified membrane surface which will attempt to repel the negatively charged BSA.

3.4. Surface stability of the modified membranes

The stability of the modified layer on the membrane surface is important for membrane to maintain hydrophilicity in practical applications. To evaluate the stability, contact angle measurements were conducted on the CA/KH560 and CA/KH590 modified membranes after being subjected to different chemical and physical stress. The stability of the modified membranes at pH = 1, 7, 12 and 14 had been investigated. Both the CA/KH560 and CA/KH590 modified membranes were immersed into acidic, neutral and alkaline solutions for 15 h. The results are shown in Fig. 10a, the CA/KH560 and CA/KH590 coatings show excellent stability under strong acidic, neutral and weak alkaline environments and there are no obvious change in WCA. However, the strong alkaline solution destroys the CA/KH560 and CA/KH590 coatings and the corresponding WCA increases to 124.5° and 121.6°, respectively. Besides, the durability of surface coatings had been studied by pure water filtration process for 72 h and corresponding operational pressure is 0.1 MPa (Fig. 10b). Although the CA/KH560 and CA/KH590 modified membranes show superior stability in pure water filtration process, hydrophilicity loss is still occurred on the membrane surface. Because the coatings

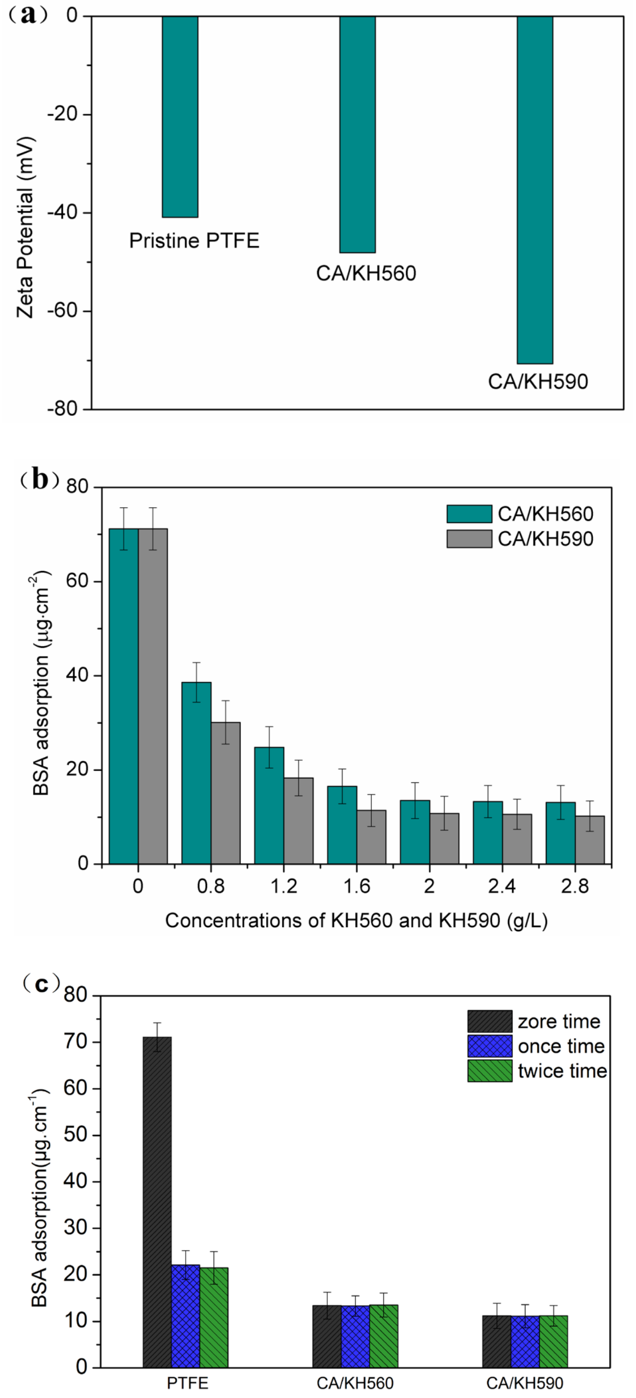

Fig. 9. (a) Zeta potential, (b) BSA adsorption of different PTFE membranes, (c) BSA adsorption-cleaning time of different PTFE membranes.

are rich in benzene rings and this structure is likely to enhance the rigidity of the hydrophilic layer which will causes coatings cracking and peeling off in long-term operation. Therefore, the stability of the coatings can be improved further by enhancing the toughness of the coatings. Maybe adding some toughening agents such as Poly(ethylene glycol) diglycidyl ether is an efficient way to solve this problem.

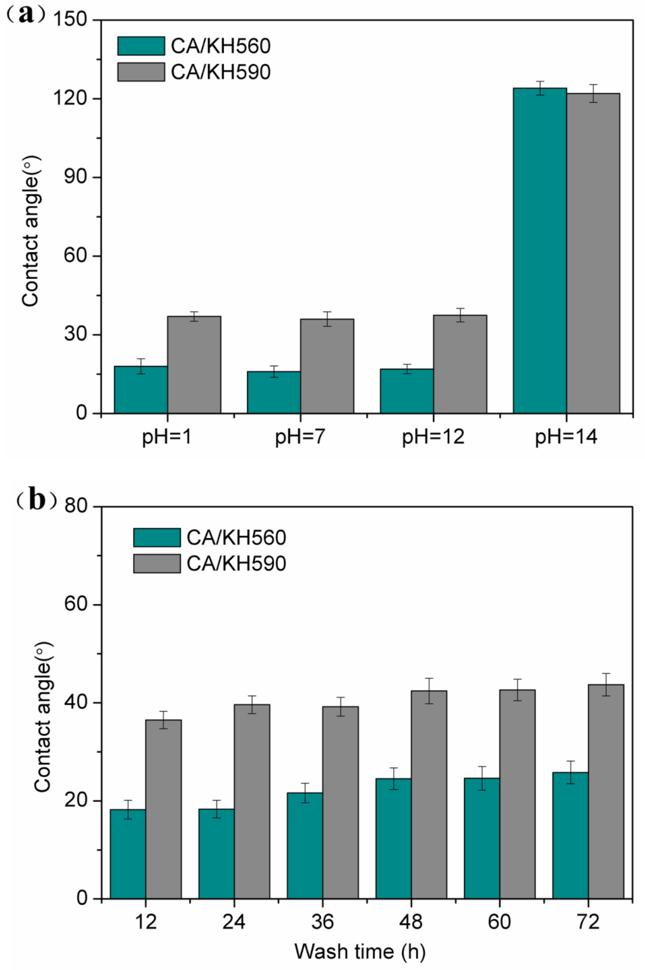

Fig. 10. (a) Water contact angle of the CA/KH560 and CA/KH590 modified membranes rinsed by solutions with different pH values for 15 h. (b) The durability of different surface coatings in pure water filtration process.

4. Conclusion

In conclusion, a facile one-step method was developed to fabricate organic-inorganic hybrid coatings on PTFE flat membranes via co-deposition of CA and silane coupling agent. Both the CA/KH560 and CA/KH590 modified membranes possess excellent wettability, high pure water flux as well as fouling resistance. Meanwhile, these membranes show superior stability under strong acidic, neutral and weak alkaline environments. It is worth mentioning that the PTFE flat membrane modified by CA and KH590 is colorless which may provide new insights into fabricating colorless coatings. Finally, the approach of co-deposition is also versatile, therefore is applicable for diverse porous membranes.

Acknowledgments

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