ACS APPLIED MATERIALS & INTERFACES

Electrically Driven Biofouling Release of a Poly(tetrafluoroethylene) Membrane Modified with an Electrically Induced Reversibly Cross-Linked Polymer

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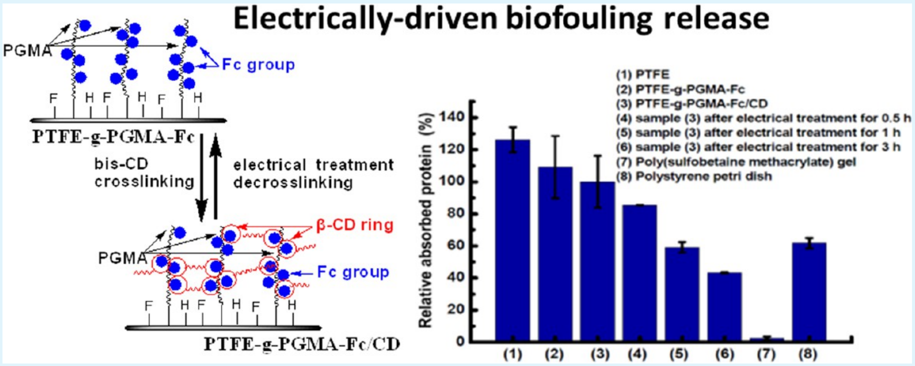

ABSTRACT: Electrically induced reversible reactions between ferrocene (Fc) and β-cyclodextrin (β-CD) groups have been utilized for preparation of poly(tetrafluoroethylene) (PTFE) membranes exhibiting electrically driven biofouling release properties. PTFE membrane is surface-modified with polymer chains possessing Fc pendant groups. The surface layer is then cross-linked with a difunctional β-CD compound by means of the Fc/β-CD complexation reaction. The electrically induced reversibly cross-linking and de-cross-linking behaviors of the surface layer of the modified PTFE membrane have been characterized with Fourier transform Infrared, X-ray photoelectron spectroscopy, and scanning electron microscopy. The surface-modified PTFE membrane has been fouled with protein absorption. Electrical treatment of the fouled membrane results in a protein detachment from the membrane surface driven by the surface structure change accompanied with the electrically induced de-cross-linking reaction of the Fc/β-CD linkages. A smart membrane exhibiting a novel cleaning technology for membrane fouling has been developed.

KEYWORDS: *membrane fouling, surface modification, poly(tetrafluoroethylene), reversible cross-linking, cyclodextrin, protein separation*

■ INTRODUCTION

Membrane-mediated filtration is widely used for materials separation. In addition to improvements on the separation efficiency, membrane fluxes, and long-term operation stability, one of the widely encountered problems to be solved for filtration membranes is fouling. The properties and efficiency of filtration membranes could dramatically decrease with fouling. As a result, it is highly expected to remove, control, or mitigate fouling effect from filtration membranes in practical applications. One of the strategies to reduce or minimize membrane fouling is optimization of operation conditions and module designs.[1−5] The efforts have shown some positive but not as satisfied results. As fouling is highly dependent on the surface properties of the membranes, tailoring the surface structures and properties of membranes have received research attention for preparation of low-fouling membranes.[6−10] The efforts focus on alteration of the interaction between the foulants and membrane surfaces to retard the fouling behavior. Removal of the foulants from the membrane surfaces could be performed to partially recover the membrane performance. Nevertheless, the recovery extent of the fouled membrane is still not high. Another strategy to solve the fouling problems for filtration membranes is to provide a more effective approach to remove the foulants from the membranes. Incorporation of photocatalysts into membranes could degrade fouling pollutants at the surfaces and inner pores of membranes, resulting in the so-called "self-cleaning" membranes.[11−15] A recent design of electrocatalytic membrane reactor combines titanium oxide (TiO_2) coated on carbon membranes.[15] The antifouling membranes with self-cleaning function show high efficiency for industrial wastewater treatment. Nevertheless, the photo-

Received: April 29, 2013
Accepted: September 18, 2013
Published: September 18, 2013

catalytic process needs ultraviolet irradiation so as to encounter some inconvenience in process design and operation.

Stimuli-responsive membranes could change their properties in response to environmental signals.[16] Membranes in response to changes of temperatures,[17−19] pH values,[20] electrical fields,[21] electrolytes,[22,23] and magnetism[24,25] have been reported. Once the foulants attach on the membrane surfaces, the changes in the membrane surface properties might provide a driving force to enable the release of the foulants from the membrane surfaces. As a result, stimuli-responsive characteristics have also been studied for improving the fouling resistance and cleaning efficiency of membranes. Yu and co-workers[26] introduced thermo-responsive properties to reverse osmosis membranes for intensifying their fouling resistance. A fouled membrane was soaked with a thermoresponsive polymer (TRP) aqueous solution below the lower critical solution temperature (LCST) of the TRP. TRP would diffuse into the fouling layer. While increasing the temperatures to above the LCST of the TRP, the TRP becomes insoluble in water so as to make the fouling layer becoming structurally loose and easily removable under rinsing. The diffusion of the TRP into the fouling layer is the key step in the process and results in some limits to this process. A modified work is coating TRPs onto membrane surfaces.[27] The change in the morphology and property of the coated TRP layer helps to removal of foulants. Nevertheless, the physically absorbed TRP layer might be washed out in the cleaning operation. Jiang et al.[28] utilized blocklike copolymers to modify PES ultrafiltration membranes. The hydrophobic segment of the blocklike copolymer ensures the copolymer being stably anchored in the membrane matrix. The pH-responsive and fluorine-containing segments of the copolymer endow the modified membranes with fouling release property. On the other hand, the pressure waves generated with the shrinking and self-collapsing behaviors of microbubbles has also been applied to induce the biofilm detachment as a cleaning technology for membrane fouling.[29]

Electrically responsive membranes could be of highly interest as electrical fields could be easily and quickly applied to the membrane systems in a large area, so as to increase the convenience of system operation. The reported studies focused on the electric-field-induced changes in the separation features of the membranes.[16,21] Electric-field-induced structure changes in the membranes could turn on and off the protein permeation through the membranes. Nevertheless, application of the electrically responsive membranes to membrane cleaning technology, to the best of our knowledge, has not been reported.

Cyclodextrin (CD) derivatives have high biocompatibility and low toxicity. Incorporation of CD derivatives into polymer systems has been reported for preparation of delivery agents for nucleic acids[30] and gene.[31] The cavity of β-cyclodextrin (β-CD) results in the ability of β-CD to complex with some groups and form supramolecules.[32−36] One of the interesting complex pairs is β-CD and ferrocene (Fc). The association and dissociation reaction between β-CD and Fc is reversible. The dissociation reaction of the β-CD/Fc complexes could be triggered with other complexation agents and charging the Fc species with reduction agents and electric current.[34−36] In this work, the electrically responsive property of the β-CD/Fc complexes has been applied to the preparation of electrically responsive membranes for membrane cleaning technology. Poly(tetrafluoroethylene) (PTFE) membranes surface modified with electrically responsive polymers have been prepared. The modified layer of the membrane possesses a cross-linked structure formed with the guest−host complexation groups of β-cyclodextrin (β-CD) and ferrocene (Fc). As dissociation of the complexes of β-CD/Fc could be performed by charging the Fc species with electric current,[34−36] the modified PTFE membranes are electrically responsive. Debonding the cross-linked structure with an electric-field provides the driving force to result in the electrically induced fouling-release properties and membrane-cleaning technology. Moreover, the fouling-release feature of the membrane is repeatable and the membrane is reworkable, as the membranes could be regenerated with recrosslinking the modified layer after the fouling-release operation. A novel and efficient approach to improve the fouling problem of filtration membranes has been demonstrated.

■ EXPERIMENTAL SECTION

Materials. Expanded porous PTFE membranes were received from Yu-Min-Tai Co. Ltd., Taiwan. The thickness and pore sizes (diameter) of the membranes are 500 and 0.24 μm, respectively. Glycidylmethacrylate (GMA, 97%) was purchased from ACROS Chem. Co. Commercial products of ferrocene carboxylic acid (Fc-COOH, Seedchem Co.), β-CD (TCI Chem. Co. Japan), and 1,6-diisocyanatohexane (HDI, ACROS) were used as received. The cross-linking agent possessing multifunctional CD groups was obtained with the reaction between HDI and β-CD in an excess of β-CD. The product is coded as bis-CD. Preparation and characterization of bis-CD has been reported in the previous paper.[36] Further characterization of bis-CD with a MALDI-TOF MS has been done in this work (Figures not shown). The result demonstrates the presence of derivatives of HDI and β-CD, including β-CD-HDI-β-CD and β-CD-HDI-β-CD-HDI.

Measurements. Fourier transform infrared (FTIR) spectra were obtained through the attenuated total reflectance method using a Perkin-Elmer Spectrum One FTIR equipped with a multiple internal reflectance apparatus and a ZnSe prism as an internal reflection element. X-ray photoelectron spectroscopy (XPS) analysis was conducted with a VG MICROTECH MT-500 ESCA (British) using an Al−Kα line as the radiation source. Scanning electron microscopy (SEM) micrographs were recorded with a Hitachi S-4800 field-emission SEM. Surface area and porosimetry measurements have been carried out with the Micromeritics ASAP 2020 accelerated surface area and porosimetry system.

Preparation of Poly(GMA) Grafted PTFE Membrane (PTFE-g-PGMA).[34] PTFE membranes in the size of 5 cm × 5 cm were treated with a hydrogen plasma (Dressler HF-Technik GmbH, Germany, model: CESAR-1310) under the conditions of a hydrogen mas flow rate of 10 standard cm^3 min^{-1}, a radio frequency of 13.56 MHz, a power of 50 W, a pressure of about 13.3 Pa, and a reaction time of 180 s. The C−F groups of the treated PTFE membranes are able to initiate atom transfer radical polymerization (ATRP) from the membrane surfaces.[33] PGMA chains were then introduced to PTFE membrane surfaces with surface-initiated ATRP of GMA. The plasma-treated PTFE were immersed in a GMA solution (15 wt %) in N,N-dimethylforamide (DMF). After being purged with argon twice, CuBr (0.202 g, 1.4 mmol), 2,2-bipyridine (0.44g, 2.8 mmol) were added to the solution. After reaction at 60 °C for 24 h, the PTFE membranes were draw out from the solution, washed with methanol and water, and then dried under vacuum at 30 °C for 24 h. The PGMA grafting yield of the product (PTFE-g-PGMA) is calculated to be 118 (μg PGMA)/(cm^2 membrane).

Preparation of Fc-Modified PTFE Membrane (PTFE-g-PGMA-Fc). PTFE-g-PGMA membranes were put in a reactor containing a solution of Fc-COOH (0.15 g, 0.65 mmol) in DMF (80 mL). The system was reacted at 80 °C under a nitrogen inlet flow for 24 h. The PTFE membranes were draw out, washed with methanol and hot water, and then dried under vacuum at 30 °C for 24 h. The ferrocene-modified PTFE-g-PGMA product was coded as PTFE-g-PGMA-Fc.

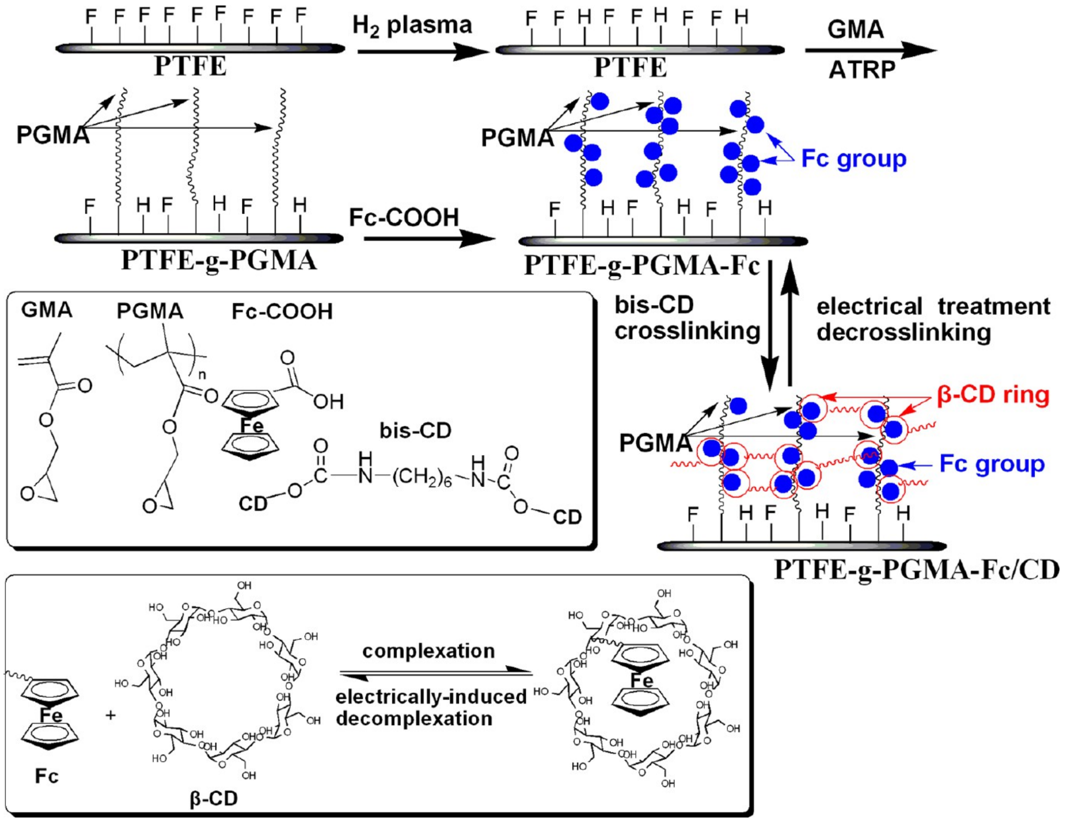

Figure 1. Synthetic route for introduction of electrically reversible cross-linked layer to PTFE membrane surface.

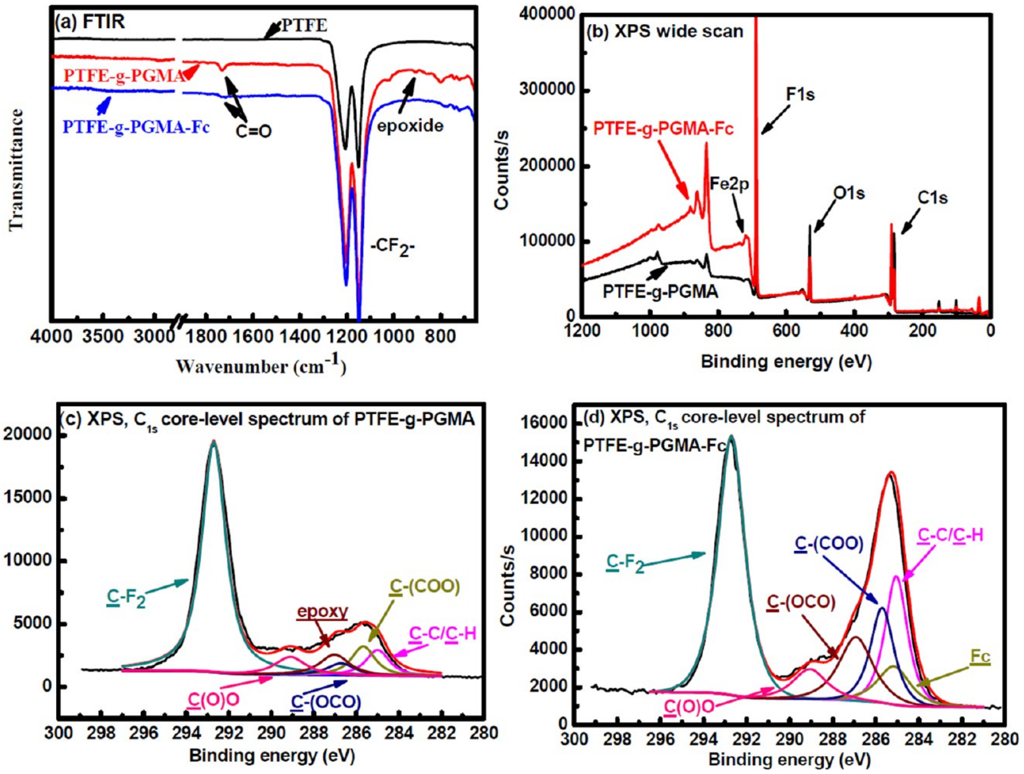

Figure 2. Characterization of PTFE membranes grafted with ferrocene modified PGMA chains with (a) FTIR spectra, (b) wide scan XPS spectra, (c, d) C_{1s} core-level XPS spectra.

Preparation of Surface-Cross-Linked PTFE Membranes (PTFE-g-PGMA-Fc/CD). The graft layer of PTFE-g-PGMA-Fc could be cross-linked through the complexation reaction between Fc and β-CD groups using bis-CD as a cross-linking agent. PTFE-g-PGMA-Fc

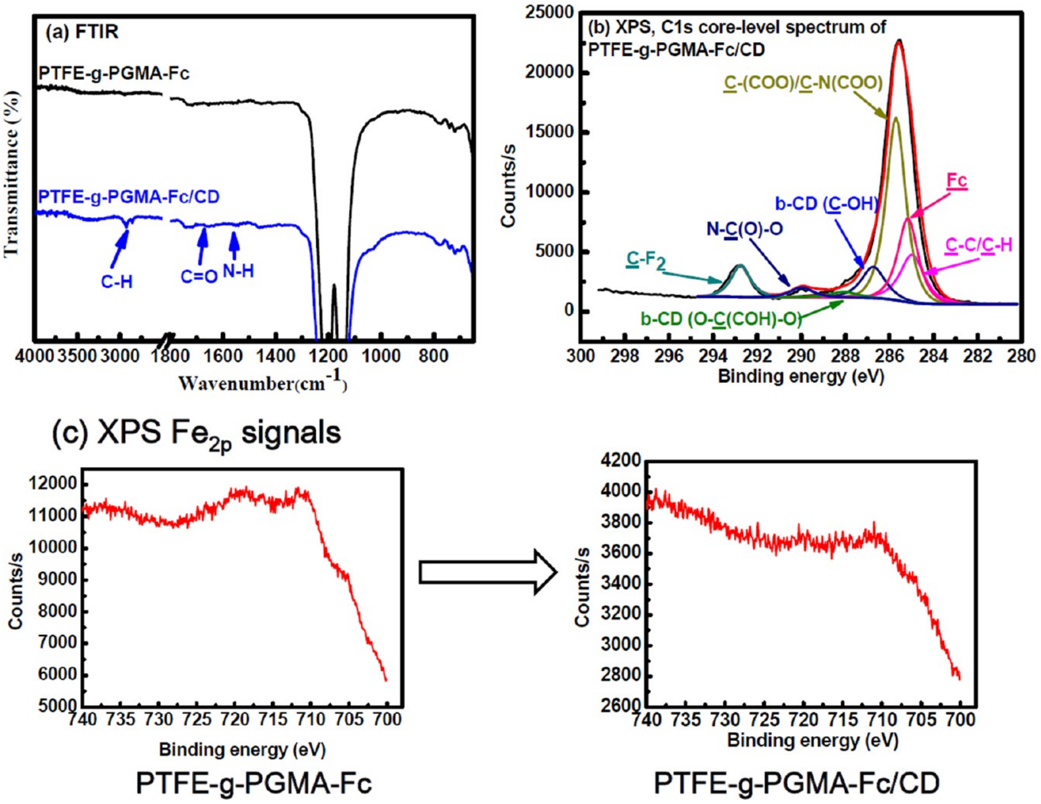

Figure 3. Characterization of bis-CD cross-linked PTFE-g-PGMA-Fc membranes with (a) FTIR spectra, (b) C_{1s} core-level XPS spectra, and (c) Fe_{2p} core-level XPS spectra.

membranes were immersed in an aqueous solution of bis-CD (1 mg mL^{-1}). The system was kept with an ultrasonic bath at room temperature for 12 h. The membranes were draw out, washed with methanol and hot water, and then dried under vacuum at 30 °C for 24 h. The obtained samples were coded as PTFE-g-PGMA-Fc/CD.

Electrical Treatment of the Protein-Absorbed Membrane. Membranes of 1.0 cm^2 surface area were first applied to protein absorption. The membranes in individual wells were equilibrated with 1000 μL of phosphate buffer saline (PBS, from Sigma Chemical) for 60 min at 37 °C, soaked in 500 μL of fibrinogen solution (the protein solution in 1 mg mL^{-1}) at 37 °C for 1 h, and then rinsed with 500 μL of PBS for 5 times. After protein absorption, some membranes were subjected to protein analysis using the enzyme-linked immunosorbent assay (ELISA) according to the protocol described in the literature.[37−39] The rest membranes were applied to the process of the electrically driven release of protein. The membranes were immersed in a PBS solution (0.01 M). An electric filed was applied to the solution using a 9 V dry cell (Panasonic Inc.). Aluminum sheets were used as the electrodes. After electrical treatment, the membranes were rinsed with a 0.01 M PBS solution slightly. The blank test was carried out with the same procedure without application of an electrical field.

■ RESULTS AND DISCUSSION

Surface-Cross-Linked PTFE Membranes (PTFE-g-PGMA-Fc/CD). Introduction of the biofouling release ability to PTFE membranes is carried out with building up an electrically driven reversibly cross-linked polymer structure on the PTFE membrane surfaces. Electrically induced de-cross-linking reaction causes the structure changes of the membrane surfaces so as to provide the driving force for removal of the foulants. Figure 1 illustrates the synthetic route for the surface-cross-linked PTFE membranes. PTFE membrane surface was first treated with a hydrogen plasma to convert some of the C−F bond to C−H bond. The plasma-treated PTFE surface has been demonstrated in the previous work[38] to be able to perform surface-initiated ATRP with the C−F groups as initiating sites. PGMA brushes were incorporated onto PTFE membrane surfaces with the surface-initiated ATRP process. Subsequently, ferrocene groups were reacted onto the grafted PGMA chains through the addition reaction between the epoxide groups of PGMA and the carboxylic acid groups of Fc-COOH. The obtained PTFE-g-PGMA-Fc membranes possess an Fc-modified PGMA layer, which could be cross-linked with a multifunctional β-CD compound through the complexation reaction between Fc and β-CD groups. Figure 2 shows the spectra recorded for the characterization of the surface structure of PTFE-g-PGMA-Fc. In the ATR-FTIR analysis, incorporation of PGMA chains to PTFE membrane surface results in the absorption peaks of C═O group and epoxide group at 1720 and 913 cm^{-1}, respectively. Reaction of Fc-COOH onto PTFE-g-PGMA was carried out with the addition reaction of epoxide and −COOH groups. The performance of this reaction is supported with the disappearance of the epoxide absorption in the FTIR spectrum of PTFE-g-PGMA-Fc. The Fc moieties of PTFE-g-PGMA-Fc are also characterized with the Fc absorption at about 1500 cm^{-1}. Moreover, the Fc moieties in PTFE-g-PGMA-Fc have also been observed with the Fe signals in the wide scan XPS spectrum (Figure 2b). Moreover, the C_{1s} core-level XPS spectra of the precursor PTFE-g-PGMA and the corresponding product PTFE-g-PGMA-Fc are shown in Figure 2c. The structure change associated with the addition reaction between Fc-COOH and the epoxide groups of PTFE-g-PGMA has been observed. The epoxide group of PTFE-g-PGMA shows the peak at a binding energy of about 287.0 eV in the C_{1s} core-level XPS spectrum of PTFE-g-PGMA. This peak is unobvious in the in the spectrum of PTFE-g-PGMA-Fc. Moreover, the Fc moieties of PTFE-g-PGMA-Fc raise the peak at about 285.1 eV in the spectrum of PTFE-g-PGMA-Fc. The results demonstrates the performance of the reaction between the epoxide groups and the −COOH groups and the successful preparation of PTFE-g-PGMA-Fc membrane. Moreover, the signals of epoxide groups are almost unobvious in the ATR-FTIR and XPS spectra of PTFE-g-PGMA-Fc, indicating the high reaction conversion between Fc-COOH and the epoxide groups of PGMA. The content of Fc groups of PTFE-g-PGMA-Fc could be calculated to be about 0.94 μmol cm^{-2}.

Cross-linking the grafted PGMA-Fc layer of the PTFE-g-PGMA-Fc membrane has been performed using bis-CD as a cross-linking agent in aqueous solution at room temperature through the complexation reaction between β-CD and Fc groups. The change of the chemical structure associating with the cross-linking reaction has been characterized with ATR-FTIR and XPS. In the ATR-FTIR spectra (Figure 3a), the appearance of the absorption peaks at about 2800−2900 cm^{-1} (C−H stretching), 1650 cm^{-1} (C═O of urethane linkage) and 1550 cm^{-1} (N−H of urethane linkage) in the spectrum of PTFE-g-PGMA-Fc/CD membrane demonstrates the incorporation of β-CD groups to the membrane surfaces. Moreover, introduction of bis-CD to the modified PTFE membranes results in the appearance of the N signal in the wide scan XPS analysis and obvious changes in the C_{1s} core-level XPS spectrum. In the C_{1s} XPS spectrum of the PTFE-g-PGMA-Fc/CD membrane (Figure 3b), the peaks corresponding to the $\underline{\mathbf{C}}$−OH groups of β-CD moiety and the urethane linkage of bis-CD structure appear at binding energy of 286.7 and 289.6 eV, respectively. The results support to the presence of β-CD moieties at the surface of the PTFE-g-PGMA-Fc/CD membrane. The intensity of the -$\underline{\mathbf{C}}F_2$ peak in the C_{1s} XPS spectrum of the PTFE-g-PGMA-Fc/CD membrane is relatively low compared to that observed with the PTFE-g-PGMA-Fc membrane. The PGMA-Fc chains tethered on the PTFE-g-PGMA-Fc membrane surface are flexible and free of motion. After being cross-linked with bis-CD, the mobility of the chains is restrained and the modified layer becomes more solid. As a result, the surface of the PTFE-g-PGMA-Fc/CD membrane is much covered with the modified PGMA layer, so as to result in the decrease in the CF_2 peak intensity. On the other hand, the Fc groups exhibit an obvious signal in the Fe_{2p} core-level XPS spectrum of PTFE-g-PGMA-Fc. This signal becomes unobvious in the spectrum of PTFE-g-PGMA-Fc/CD (Figure 3c). The result provides additional support to the performance of the cross-linking reaction basing on the Fc/β-CD complexation.

The morphology of the membrane surfaces have been observed with a SEM. As shown in Figure 4, pristine PTFE membrane shows a typical porous morphology. Introduction of PGMA chains through the surface-initiated polymerization results in the morphology with PGMA portion covering on the membrane surface. The surface morphology does not show an obvious change after reacting with Fc-COOH. Nevertheless, cross-linking the PTFE-g-PGMA-Fc membrane with bis-CD makes the PGMA chains more restrained. As a result, the surface morphology of PTFE-g-PGMA-Fc/CD membrane shows a solid polymeric layer covering on the porous PTFE substrate.

Electrically Driven De-Cross-Link of the Surface Layer of PTFE-g-PGMA-Fc/CD Membranes. The surface layer of PTFE-g-PGMA-Fc/CD membrane possesses a cross-linked structure linked with the Fc/CD complexes. As the Fc/CD complexes perform a dissociation reaction with electric current,[34−36] the surface layer of PTFE-g-PGMA-Fc/CD membrane could perform the electrically driven de-cross-linking reaction. As shown in Figure 5, the structural change of PTFE-g-PGMA-Fc/CD sample associating with an electrical treatment for 3 h could be characterized with the C_{1s} core-level XPS spectra. The decomplexation reaction of the Fc/CD complexes results in the release of bis-CD from the membrane surface. As a result, the intensities of the peaks of the $\underline{\mathbf{C}}$−OH groups (286.7 eV) of β-CD moiety and the urethane linkage (289.6 eV) of bis-CD decrease with the electrical treatment of the sample. Moreover, the chain flexibility of the grafted polymer layer also increases with the de-cross-linking reaction. As a result, electrical treatment also result in the increase of the peak intensity of the -$\underline{\mathbf{C}}F_2$ group in the C_{1s} core-level XPS spectrum of PTFE-g-PGMA-Fc/CD. As structural change of the membrane has not been observed with the sample in the blank test without electrical treatment, the removal of bis-CD compounds from the membrane surface is induced with the electrically triggered dissociation reaction of Fc/CD complexes. As a result, the electrically treated PTFE-g-PGMA-Fc/CD sample should possess similar chemical structure of PTFE-g-PGMA-Fc. This has been demonstrated with the spectra shown in panels a and c in Figure 5, as the electrically treated PTFE-g-PGMA-Fc/CD and PTFE-g-PGMA-Fc show similar C_{1s} core-level XPS spectra. On the other hand, the cross-linking and de-cross-linking of the surface layer of the PTFE-g-PGMA-Fc sample is repeatable. The performance of the recrosslinking reaction on the surface layer of the de-cross-linked PTFE-g-PGMA-Fc/CD membrane is still supported with the C_{1s} core-level XPS spectrum (Figure 5d), which is different from the spectrum of the de-cross-linked sample but similar to the spectrum of the first cross-linked sample.

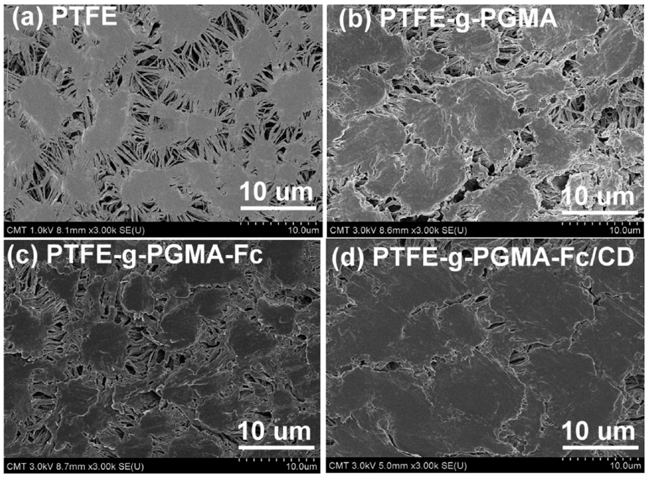

Figure 4. SEM micrographs of pristine and surface-modified PTFE membranes: (a) pristine PTFE membrane, (b) PGMA-modified PTFE membrane (PTFE-g-PGMA), (c) PTFE membrane possessing ferrocene groups (PTFE-g-PGMA-Fc), and (d) surface-cross-linked PTFE membrane (PTFE-g-PGMA-Fc/CD).

Figure 6 shows the SEM micrographs recording the changes of the surface morphology of PTFE-g-PGMA-Fc/CD membrane in the cross-linking and de-cross-linking cycles. Compared to the fully covered surface of PTFE-g-PGMA-Fc/CD membrane, the electrically induced de-cross-linked sample shows a surface partially covered with the grafted layer associated with the loose un-cross-linked chains. Meanwhile,

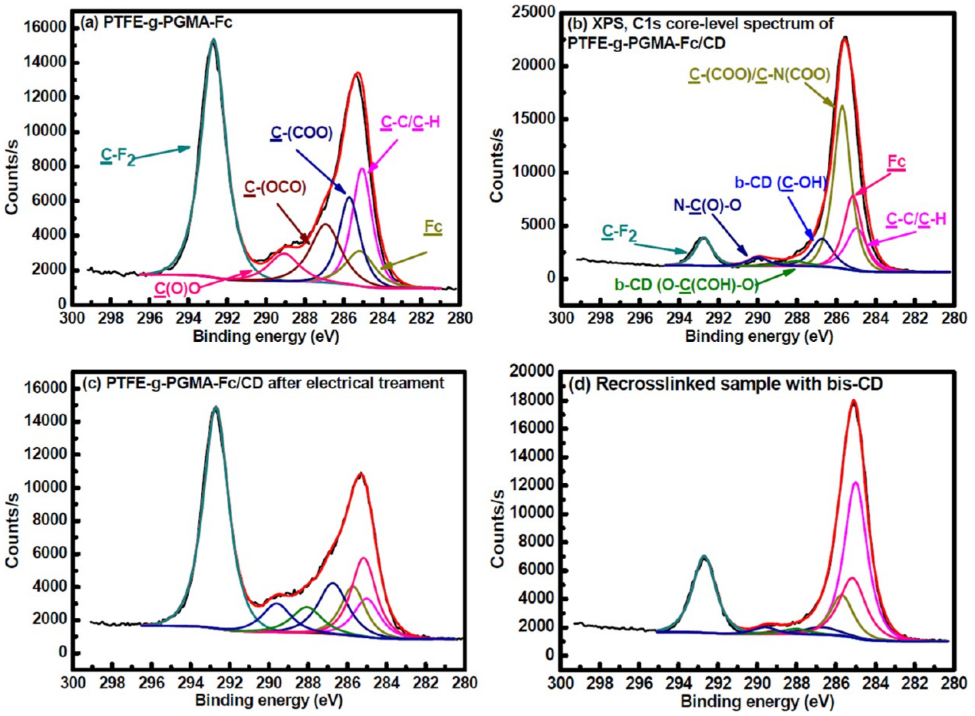

Figure 5. C_{1s} core-level XPS spectra monitoring on the electrically induced reversibly cross-linking and cross-linking behavior of the surface layer of PTFE-g-PGMA-Fc membrane.

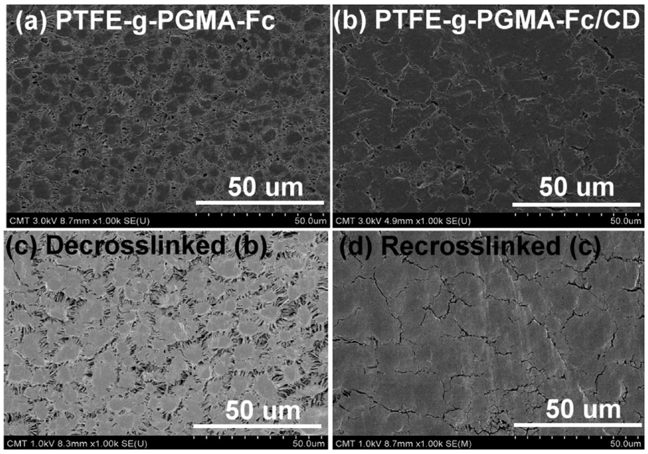

Figure 6. SEM micrographs of surface-modified PTFE membranes showing the morphology changes with the reversibly cross-linking-de-cross-linking process: (a) PTFE membrane possessing ferrocene groups, (b) sample a after being cross-linked with bis-CD compounds (PTFE-PGMA-Fc/CD), (c) de-cross-linked sample b after electrical treatment, and (d) sample c after being recrosslinked with bis-CD compounds..

recrosslinking the surface layer results in the surface morphology changing back to the style similar to the morphology observed with the original PTFE-g-PGMA-Fc/CD membrane. The structural changes of the membranes in the cross-linking and de-cross-linking process also result in the change of surface contact angles. The water contact angle of PTFE-g-PGMA-Fc membrane surface is about 108°, which decreases to about 96° after cross-linking with bis-CD. De-cross-linking the sample recovers the hydrophobicity of the sample with a water contact angle of 113°. The above results and discussion demonstrate the surface layer of PTFE-g-PGMA-Fc/CD membrane is electrically responsive. The cross-linking complexation reaction and the de-cross-linking dissociation reaction could be carried repeatedly.

The surface area and pore sizes of the membranes have been measured with a BET instrument. Pristine PTFE membrane exhibits a pore size and a surface area of 540 nm and 2.9 $m^2\ g^{-1}$, respectively. Surface functionalization does not result in an obvious change on the data. After cross-linking, the pore size and surface area of PTFE-g-PGMA-Fc/CD membrane decreases to 390 nm and 2.3 $m^2\ g^{-1}$, respectively. After electrical treatment to de-cross-link the surface layer of the membrane, the pore size and surface area increase to 450 nm and 2.5 $m^2\ g^{-1}$, respectively. The changes of the pore size and surface area of the membranes associating with the treatment process also support to the performance of cross-linking and de-cross-linking behaviors of the surface layer of the membranes.

Electrically Driven Removal of Proteins Fouling the Membrane. The electrically induced change of the surface structures of PTFE-g-PGMA-Fc/CD membrane has been applied to detach fouling proteins from the membrane surfaces for development of a novel cleaning technology for membrane fouling. PTFE-g-PGMA-Fc/CD membranes were put in a fribingen solution (1 mg mL^{-1}) for 1 h for absorption of the protein on the membrane surface. After being washed, some of the membranes were put in a PBS solution (0.01 M), electrically treated with a 9 V cell for various periods of time, and rinsed with a PBS solution. The relative amounts of proteins absorbed on the membrane surfaces were determined with the ELISA protocol using polystyrene Petri dish (PS-dish) as a reference.[8,38,39] The result is shown in Figure 7. As we do not incorporate any antiprotein-absorption polymer chains (such as poly(ethylene glycol)) to the membrane surface, the pristine PTFE and the surface-modified PTFE-g-PGMA-Fc/CD membranes have higher amounts of protein absorption, which are about 1.6 times of the amount of protein absorbed on

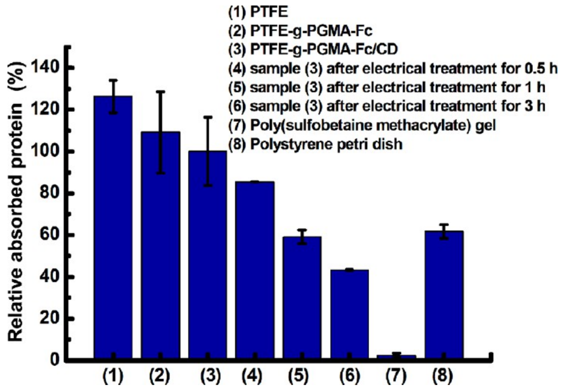

Figure 7. Relative amounts of protein absorbed on different PTFE membrane surfaces. The data obtained with poly(sulfobetaine methacrylate) gel and polystyrene Petri dish is included for comparison.

the PS-dish. The high amounts of the absorbed protein could be attributed to the hydrophobicity of the PTFE-based membranes. Electrical treatment of the membrane shows an effective result to reduce the amount of the absorbed protein because of the performance of the electrically induced de-cross-linking reaction on the membrane surface. The sample with a 3 h of treatment time has a relatively small amount of absorbed protein, which is about 45% compared to the untreated membrane and 75% compared to the PS-dish. It is noteworthy that the electrically triggered de-cross-linking reaction of PTFE-g-PGMA-Fc/CD membrane should provide the driving force for the protein release behavior, as it was not observed with the blank test (under the same process without electrical treatment).

Some efforts have been done to incorporate antiprotein−absorption surface to the membranes. The approaches change the membrane surface properties so as to turn the absorption of proteins from irreversible to reversible. The absorbed protein could be washed out with hydraulic cleaning result. Nevertheless, the remained irreversibly absorbed proteins still reduce the membrane fluxes seriously and results in membrane fouling finally. It is obvious that a high-performance antifouling membrane could be obtained with combination of the technique reported in this work and the approaches of incorporation of an anti-protein-absorption surface to membranes. For example, poly(ethylene glycol) and other suitable polymer chains could be introduced to the PTFE-g-PGMA-Fc/CD membranes with simple chemical reactions. Continuing work is still under investigation.

■ CONCLUSION

An electrically driven reversibly cross-linked polymer structure has been incorporated on PTFE membrane surface with surface-initiated polymerization and post modification reactions. The surface-modified PTFE membrane becomes an electric-responsive membrane. The changes of the surface structures of the modified PTFE membrane could be reversibly performed with an electrical treatment associating with the cross-linking and de-cross-linking reactions of the surface polymeric layer. The structural change of the surface layer is able to induce the detachment of protein absorbed on the membranes and perform an action of biofouling release. A novel smart membrane and a cleaning technology for membrane fouling have been developed. Further studies could focus on incorporating anti-protein-absorption polymeric chains to the membranes to result in the antifouling and easy-cleaning membranes for bioseparation.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the Ministry of Economic Affairs (Grant 102-EC-17-A-09-S1-198) and the National Science Council (NSC 101-2623-E-007-013-IT) for financial support on this work.

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