

Mussel-inspired Modification of Microporous Polypropylene Membranes for Functional Catalytic Degradation^{*}

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Abstract In this manuscript, an easy method of anchoring Au nanoparticles onto a polypropylene (PP) membrane to prepare a composite Au-PP membrane with catalytic activity was demonstrated. The surface of the PP membrane was first modified with a primary amine by mussel-inspired dopamine polymerization. Then, the modified PP membrane was used to reduce chloroauric acid to anchor Au nanoparticles onto the surface, forming a Au-PP membrane. The surface morphology and composition of the modified PP membrane were characterized with SEM, ATR-FTIR and XPS. The catalytic activity of the Au-PP membrane was also evaluated by the degradation of a model dye solution of methylene blue. The fabricated membrane shows excellent catalytic performance, and the catalytic activity can be effectively regenerated.

Keywords: Dopamine; Microporous polypropylene membrane; Au nanoparticles; Catalytic degradation.

INTRODUCTION

Porous PP membranes have been widely studied and used because of their excellent characteristics, such as oxidative resistance, corrosion resistance, and low cost^[1]. However, this type of membrane is hard to combine with other materials due to the low surface energy of the PP material. Therefore, surface modification of PP membranes has been a popular issue in recent years^[2]. Traditional modification methods include physical coating and chemical modification^[3]. The physical coating method is simple and easy to realize, and it barely damages the membrane^[4–6]. For example, Lee *et al.* adhered particles such as Al₂O₃/SiO₂ ceramic materials onto the PP membrane to increase its thermal shrinkage resistance^[4, 5]. However, the coating layer obtained with this type of method is easy to strip off during use, which would lead to performance degradation or loss of function. Compared with physical coating, chemical modification is much more stable. The modified molecules react with the membrane surface to form a new modified surface^[7, 8]. Materials such as acrylic acid^[9], acrylamide^[10], poly(ethylene glycol) (PEG)^[11], *N*-isopropyl acrylamide (NIPAAm)^[12, 13] and *N,N*-dimethylaminoethyl methacrylate (DMAEMA)^[14] have been introduced to improve the properties of PP membranes by chemical methods. Mathias *et al.* used a UV irradiation method and the cross-linker *N,N'*-methylenebis(acrylamide) to graft 2-acrylamido-2-methylpropanesulfonic acid onto the membrane to obtain molecularly imprinted polymer membranes, which can be used for the determination of herbicides in water^[15]. Shan *et al.* introduced the method

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of reversible addition-fragmentation chain transfer polymerization and click chemistry to modify a PP membrane with acid alkyne-terminated poly(2-acrylamido-2-methyl propane sulfonic acid)) for protein fouling mitigation^[16]. However, the chemical modification method is prolix to achieve and even destroys the membrane.

Mussel-inspired surface chemistry has attracted much attention for its simplicity, versatility and wide scope of application^[17–19]. Dopamine is a type of catechol with two neighboring (ortho-)hydroxyl groups, and it easily self-polymerizes to form polydopamine^[20]. It has become a potential method for the surface modification of various materials^[19, 21, 22]. Messersmith *et al.* modified the surface of a nitrocellulose film, a coin, a three-dimensional plastic object and a Si substrate with dopamine using a simple dip-coating method^[21]. Lee *et al.* produced a super-hydrophobic surface *via* a soft-lithographic technique with mussel-inspired dopamine^[23]. Zhu *et al.* introduced dopamine to modify polyethylene (PE), poly(vinylidene fluoride) and poly(tetrafluoroethylene) porous membranes and then tested their durabilities, which were found to be excellent^[24, 25]. Choi and co-workers treated a PE membrane with dopamine to obtain an excellent battery separator that had a high cycle life and thermo-stability^[26, 27]. Zhang *et al.* embedded magnetic Fe₃O₄ nanoparticles into polydopamine by self-assembly for the specific capture of protein^[28]. Compared with the physical coating method, the strong adhesion of the catechol structure made the chemical modification much more stable and less damaging to the membrane. The best and brightest advantage of the chemical modification method is the introduction of reactive groups, as the two neighboring (ortho-)hydroxyl groups and amine group react very easily with other functional molecules. Wei *et al.* embedded carbon nanotubes with dopamine and fabricated their surfaces with hydrophilic/hydrophobic groups *via* Michael addition reactions^[29]. Zhu *et al.* introduced heparin onto a PE porous membrane *via* the adhesion and covalent bonding of dopamine, which made the membrane hemocompatible^[30]. The dopamine and its derivatives are expensive, which has limited the application range. Recently, Wang *et al.* replaced dopamine with low cost catechol and polyamine, and successfully modified hydrophobic PP separator to be hydrophilic, which would greatly promote development of the mussel inspired modification^[31].

Herein, we report an easy method to functionalize a PP membrane with catalytic Au nanoparticles *via* mussel-inspired dopamine modification. The modified membrane shows an efficient catalytic ability in the degradation of methyl blue. Furthermore, the membrane is promising for application in sewage water treatment through the infiltration process.

EXPERIMENTAL

Membrane Materials and Chemicals

Commercial porous PP membranes (CangzhouMingzhu Plastic Co., Ltd., China) with a thickness of 20 μm were used. All membrane samples were cut into disks with diameters of 60 mm. 3,4-Dihydroxyphenethylamine (dopamine) and tris(hydroxymethyl)aminomethane (Tris) were purchased from Aladdin (China). A Tris-HCl buffer solution (10.0 mmol/L, pH = 8.5) was prepared according to the method described in previous publications^[32]. Methylene blue (MB) was purchased from Jingke Fine Chemical (China). Ethanol, chloroauric acid and sodium borohydride were purchased from Beijing Chemical Works (China). All of the reagents were used as received.

Dopamine Modification of PP Membranes

The dopamine-modified PP membranes were prepared *via* floating membranes onto a dopamine Tris-HCl buffer solution at room temperature for a certain number of hours to polymerize. After the dopamine had polymerized, the membranes were taken out and washed with deionized water to obtain the dopamine-modified PP membranes. The weights of the membrane samples were measured after drying at 40 °C in a vacuum oven.

Physical and Chemical Characterization of the Membranes

The self-polymerizing content of the dopamine on the PP membrane was calculated using Eq. (1):

$$I = \frac{m_g - m_0}{s} \quad (1)$$

where m_g and m_0 are the weights of the PP membrane after and before dopamine modification, respectively, and s is the surface area. The morphologies of the membranes were observed by scanning electronic microscopy (SEM) (Hitachi S4800, Japan) after gold spraying. The water permeabilities of the membranes were obtained *via* an ultrafiltration cup (pressure: 0.2 MPa, area: 0.96 cm²). The chemical composition of the surface layer was characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet NEXUS) and X-ray photoelectron spectroscopy (XPS, VG Scientific Ltd., UK). The XPS data were calibrated with the C1s hydrocarbon peak at 284.80 eV to eliminate surface charge effects.

Immobilization of Catalytic Au Nanoparticles onto the PP Membranes

The primary amine of the dopamine-modified PP membrane could be used as a reductant. Herein, it was used to reduce the chloroauric acid to adhere Au nanoparticles onto the PP membrane^[31, 33], which was catalytically active. The catalytic Au-PP membranes were obtained by immersing the dopamine-modified PP membranes into chloroauric acid for 24 h at room temperature. Then, they were taken out, rinsed with deionized water and dried at 40 °C in a vacuum oven. The procedure is shown in Fig. 1.

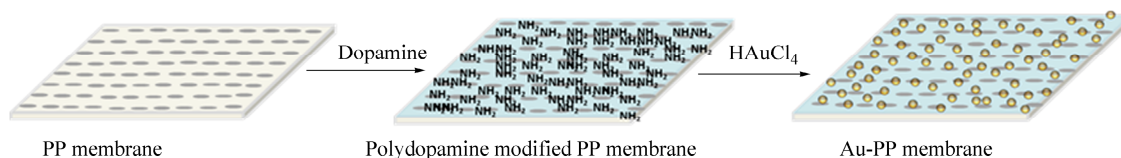


Fig. 1 Schematic illustration of the preparation of functional catalytic Au-PP membrane

Catalytic Reductive Ability of the Au-PP Membranes

The catalytic reductive ability of the Au-PP membranes was evaluated with a model dye solution of methylene blue. The Au-PP membranes were fixed in the ultrafiltration cup to infiltrate the methylene blue stock solution. Because the Au nanoparticles displayed catalytic reductive activity, the methylene blue would degrade, and the concentration in the filtrate would be lower than that in the stock solution. The concentration was measured with an ultraviolet-visible spectrophotometer (Lambda 900, PerkinElmer). The absorbance value was used to calculate the degradation ratio D according to Eq. (2):

$$D = \frac{T_x - T_0}{T_0} \times 100\% \quad (2)$$

where T_0 is the absorbance value of the original stock solution and T_x is the absorbance value of x mL of filtrate.

RESULTS AND DISCUSSION

Preparation of the Modified Membranes

Analysis of the self-polymerized content

The PP membranes were modified by floating them on a dopamine Tris-HCl buffer solution at room temperature for a certain number of hours to obtain the dopamine-modified PP membranes. Dopamine solutions at three concentrations (*i.e.*, 1.0 mg·mL⁻¹, 1.5 mg·mL⁻¹ and 2.0 mg·mL⁻¹) were used to prepare modified PP membranes with various dopamine self-polymerized contents. The self-polymerization kinetics is shown in Fig. 2. For each concentration, the self-polymerized content increased linearly with the reaction time. At a concentration of 1.0 mg·mL⁻¹, the increase in the rate was 1.61 μg·cm⁻²·h⁻¹. After reacting for 24 h, the polymerized content was 49 μg·cm⁻². At concentrations of 1.5 and 2.0 mg·mL⁻¹, the increases in the rates were 1.74 and 2.34 μg·cm⁻²·h⁻¹, respectively. There was a greater increase in the rate with increasing concentrations as expected. After reacting for 24 h, the polymerized contents were 83 and 113 μg·cm⁻², respectively. The self-polymerized process could

be followed from the color and wetting ability. As dopamine self-polymerized, the color of the PP membrane changed from white to brown uniformly and the water contact angle reduced from 102.5° to 60° , which meant that PP membrane had been modified to be hydrophilic. The membranes that had reacted for 24 h were further characterized.

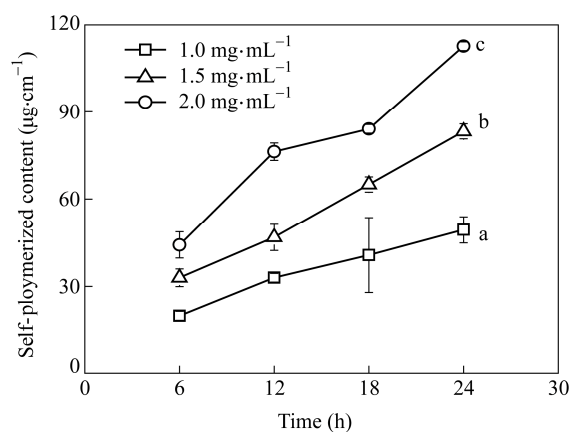


Fig. 2 The effect of dopamine concentration and time on the self-polymerized content: (a) $1.0 \text{ mg}\cdot\text{mL}^{-1}$, (b) $1.5 \text{ mg}\cdot\text{mL}^{-1}$ and (c) $2.0 \text{ mg}\cdot\text{mL}^{-1}$

Surface chemical composition analysis

The surface chemical compositions of the bare PP membrane and the dopamine-modified PP membranes were confirmed by ATR-FTIR as shown in Fig. 3(a). For the bare PP membrane, the strong absorbance at approximately 2900 cm^{-1} is attributed to the aliphatic C—H stretching vibrations of CH_2 , and the absorbance at 1400 cm^{-1} is caused by in-plane bending. Compared with the bare PP membrane, characteristic absorbance bands of self-polymerizing dopamine appear in the range of 1620 to 1280 cm^{-1} for the dopamine-modified PP membranes, such as bands at 1617 cm^{-1} (superposition of N—H bending and phenolic C—C stretching), 1610 cm^{-1} (C=C resonance vibrations in aromatic rings and N—H bending vibrations) and 1510 cm^{-1} (N—H shearing vibrations). The presence of characteristic absorbance bands of self-polymerizing dopamine suggests that dopamine has successfully polymerized onto the PP membrane.

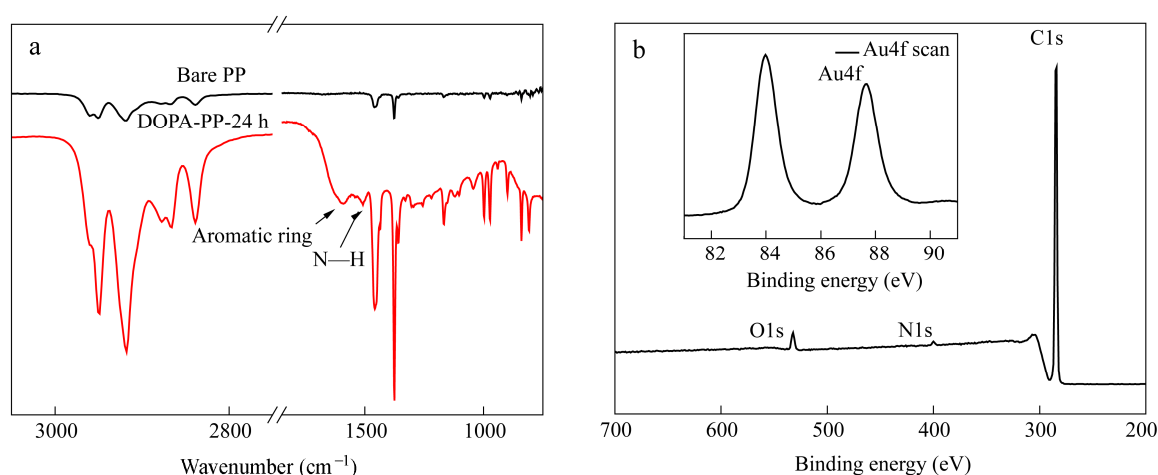


Fig. 3 (a) The ATR-FTIR spectra of PP membranes and (b) XPS spectra of the Au-PP membrane

The surface elements of the Au-PP membrane were characterized by XPS. As shown in Fig. 3(b), because the modified membrane was composed of PP, the C1s peak at 284.8 eV belongs to carbon atoms of the polymer chain. At the same time, obvious peaks of oxygen (O1s) at 532.3 eV and nitrogen (N1s) at 400.1 eV were found, which could be attributed to the self-polymerized dopamine adhered onto the PP membrane. Additionally, as shown in the enlarged area, a peak at 84.2 eV belonging to gold (Au4f) was found, which meant that chloroauric acid had been successfully reduced by the primary amine of the polymerized dopamine and Au nanoparticles had formed on the dopamine-modified PP membrane to obtain the Au-PP membrane.

Morphologies of the membranes

The surface morphologies of the bare and modified PP membranes were observed by SEM as shown in Fig. 4. The bare PP membrane has many oval-shaped micropores between lamellar stacks and separated by the fibrils, which originate from the crazing of samples under uniaxial stretching. The oval-shaped micropores were approximately 200 nm along their major axis and 40–60 nm along their short axis, as shown in Fig. 4(a). After the dopamine self-polymerization, the surface morphologies changed gradually as shown in Figs. 4(b)–4(d). For the modified PP membrane with a polymerized content of $49 \mu\text{g}\cdot\text{cm}^{-2}$, no obvious change was observed, as shown in Fig. 4(b). As the polymerized content increased to $85 \mu\text{g}\cdot\text{cm}^{-2}$, an obvious layer of dopamine could be observed to be polymerized on the membrane surface. The lamellar stack became thicker, and the sizes of the oval-shaped micropores obviously decreased. Parts of the micropores were thoroughly covered, as indicated by the arrows in Fig. 4(c). As the polymerized content further increased to $113 \mu\text{g}\cdot\text{cm}^{-2}$, a thicker layer of polymerized dopamine was formed on the PP membrane. Both the size of the lamellar stack and the size of the fibrils were increased, which led to a further decrease in the pore size as shown in Fig. 4(d). Because the water flux was determined by the pore size, the decrease in the pore size by dopamine polymerization might greatly undermine the water flux of the membrane.

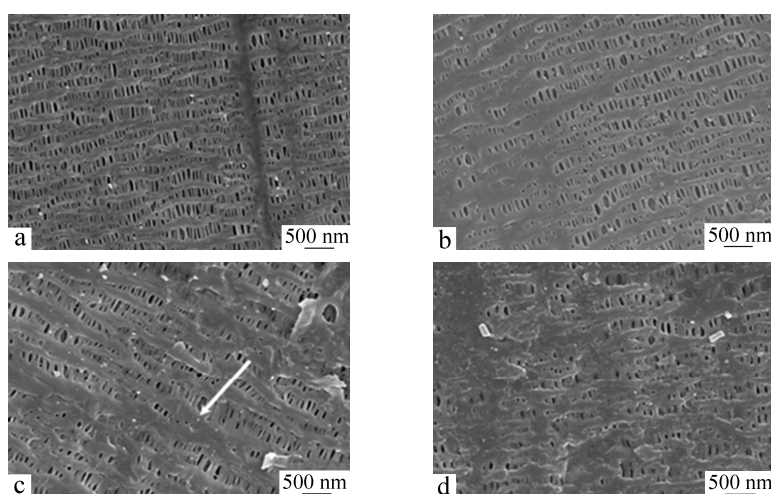


Fig. 4 Surface morphologies of (a) PP membrane, and PP membranes with polymerized dopamine of different amounts: (b) $49 \mu\text{g}\cdot\text{cm}^{-2}$; (c) $85 \mu\text{g}\cdot\text{cm}^{-2}$ and (d) $113 \mu\text{g}\cdot\text{cm}^{-2}$

The morphology of the Au-PP membranes was also observed with SEM as shown in Fig. 5. The Au nanoparticles formed on the lamellar stack and the inter-fibril regions. The size of the Au nanoparticles was about 55 nm when the polymerized dopamine content was $49 \mu\text{g}\cdot\text{cm}^{-2}$ as shown in Fig. 5(a). As the polymerized content increased to 85 and $113 \mu\text{g}\cdot\text{cm}^{-2}$, no obvious size increasing effect was observed and the size of the Au nanoparticles was about 100 nm as shown in Figs. 5(b)–5(c). However, the number of the Au nanoparticles increased obviously with the content of polymerized dopamine. The content of Au nanoparticles on Au-PP membranes was determined by weight increase method. It was shown that there were $131 \mu\text{g}\cdot\text{cm}^{-2}$, $135 \mu\text{g}\cdot\text{cm}^{-2}$ and $138 \mu\text{g}\cdot\text{cm}^{-2}$ Au nanoparticles on the Au-PP membranes when the polymerized dopamine on PP membranes

was $49 \mu\text{g}\cdot\text{cm}^{-2}$, $85 \mu\text{g}\cdot\text{cm}^{-2}$ and $113 \mu\text{g}\cdot\text{cm}^{-2}$ respectively. It seemed that more polymerized dopamine would lead to more Au nanoparticles.

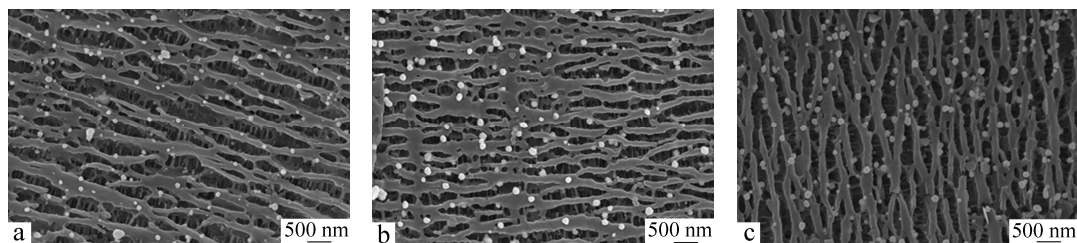


Fig. 5 Surface morphologies of Au-PP membranes with polymerized dopamine content of (a) $49 \mu\text{g}\cdot\text{cm}^{-2}$; (b) $85 \mu\text{g}\cdot\text{cm}^{-2}$ and (c) $113 \mu\text{g}\cdot\text{cm}^{-2}$

Water Permeabilities of the Modified Membranes

The water permeability is an important index for filter membranes. Before testing, all of the membranes were pre-wetted with ethanol and balanced for 24 h. The water permeability for the bare PP membrane was approximately $300 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. After modification, polymerized dopamine adhered to the membrane surface and skeleton, so the water flux for the functionalized PP membrane obviously decreased. The flux decreased with the reaction time, as shown in Fig. 6. After reacting in a dopamine solution for 6 h, the water flux decreased to $220 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. The water flux decreased at a rate of $5.15 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ with the increase in the reaction time. After reacting for 24 h, the flux decreased to $129 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. Higher dopamine concentrations led to a further decline in the water flux. After reactions in $1.5 \text{ mg}\cdot\text{mL}^{-1}$ and $2.0 \text{ mg}\cdot\text{mL}^{-1}$ dopamine solutions for 6 h, the water fluxes were 199 and $137 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively, which were much less than that in the $1.0 \text{ mg}\cdot\text{mL}^{-1}$ dopamine solution. The fluxes decreased with the reaction time at rates of 4.88 and $3.53 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. After 24 h of reaction time, the fluxes were 114 and $74 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively.

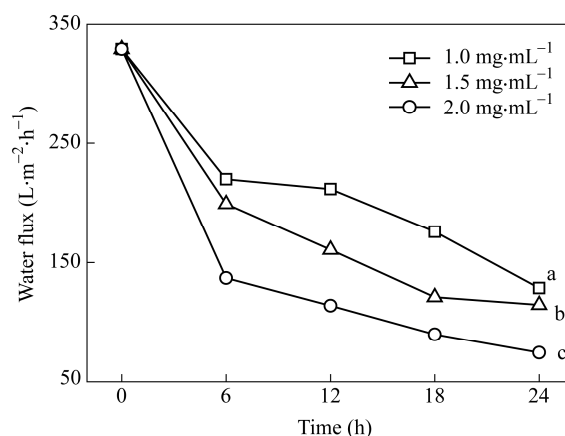


Fig. 6 The water permeability of modified membranes with dopamine concentrations of (a) $1.0 \text{ mg}\cdot\text{mL}^{-1}$, (b) $1.5 \text{ mg}\cdot\text{mL}^{-1}$ and (c) $2.0 \text{ mg}\cdot\text{mL}^{-1}$

Catalytic Degradation Ability of the Au-PP Membrane

Due to the reductive performance of the primary amine of dopamine, chloroauric acid was reduced to form Au nanoparticles on the modified PP membrane with catalytic activity. To evaluate the catalytic activity of the Au-PP membrane with $113 \mu\text{g}\cdot\text{cm}^{-2}$ polymerized dopamine, methylene blue was introduced as the catalysant, and the UV absorbance of the filtrate was monitored, as shown in Fig. 7(a). Two absorbance bands at 610 nm and 665 nm were attributed to the absorbance of methylene blue, and the absorbance value at 665 nm was used to compare the catalytic activities of the various membranes. The concentration of the original stock solution was

$100 \mu\text{mol}\cdot\text{L}^{-1}$, and the corresponding absorbance value was 2.47. In the first 1 mL of filtrate, the absorbance value was near 0, which meant that almost all of the methylene blue could be degraded by the Au nanoparticles on the PP membrane. With an increase in the filtrate volume, the catalytic efficiency decreased, and the absorbance value gradually increased. When the filtrate volume reached 51 mL, the absorbance value was 0.44, corresponding to a concentration of $17.8 \mu\text{mol}\cdot\text{L}^{-1}$. As the filtrate volume increased to 101 mL, the absorbance value reached 0.42. However, the concentration of methylene blue was not greatly increased and remained almost constant at $17.0 \mu\text{mol}\cdot\text{L}^{-1}$. To eliminate the effect of self-degradation by sodium borohydride without Au nanoparticles, the absorbance value of the original stock solution was monitored for the same amount of time that was needed for 1 mL, 51 mL and 101 mL to infiltrate. The absorbance value was almost constant as shown in Fig. 7(b), which meant that the self-degradation was negligible. Thus, the decrease in the methylene blue concentration was due to the catalytic activity of the Au nanoparticles attached onto the surface of the PP membrane, and it was found that they possessed a high catalytic activity. The catalytic activity was comparable with those reported in the literatures^[34–37].

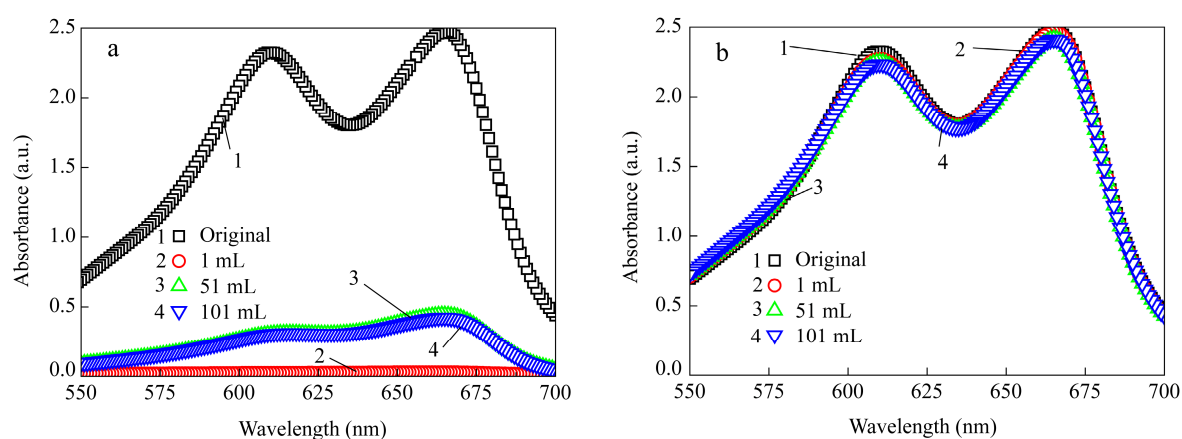


Fig. 7 The changes of UV absorbance of filtrate (a) and stock solution (b) with different filtration time

The methylene blue degradation ratios of the catalytic Au-PP membranes with 49, 85 and $113 \mu\text{g}\cdot\text{cm}^{-2}$ polymerized dopamine were calculated according to Eq. (2), and the results are shown in Fig. 8. The degradation ratio decreased as the filtrate volume increased, and then, it gradually stabilized to a certain ratio. In the first 10 mL of filtrate, a degradation ratio of 95% could be reached. When the filtrate volume was less than 20 mL, 90% of the methylene blue could still be degraded. As the filtrate volume increased to more than 20 mL, the degradation ratio decreased greatly, and it reached a constant value at a filtrate volume greater than 40 mL. The degradation ratios for the three types of Au-PP membranes with 49, 85 and $113 \mu\text{g}\cdot\text{cm}^{-2}$ polymerized dopamine were stable at approximately 72%, 80% and 85%, respectively. The attachment of more polymerized dopamine would lead to more primary amines on the PP membrane; therefore, more Au nanoparticles would form, and a higher degradation ratio would be achieved.

The recyclability of the functionalized Au-PP membrane with $113 \mu\text{g}\cdot\text{cm}^{-2}$ polymerized dopamine was also evaluated. The membrane was first fixed in the ultra-filtration cup to let the methylene blue solution infiltrate. After 41 mL of filtrate was collected, the membrane was taken down and rinsed with alcohol to regenerate. This procedure was repeated four times, and the results are shown in Fig. 9. For each cycle, the absorbance value increased with increasing filtrate volumes. After rinsing, a very low absorbance value could be obtained. This behavior was repeatable, which meant that this type of functionalized Au-PP membrane had very good regeneration performance.

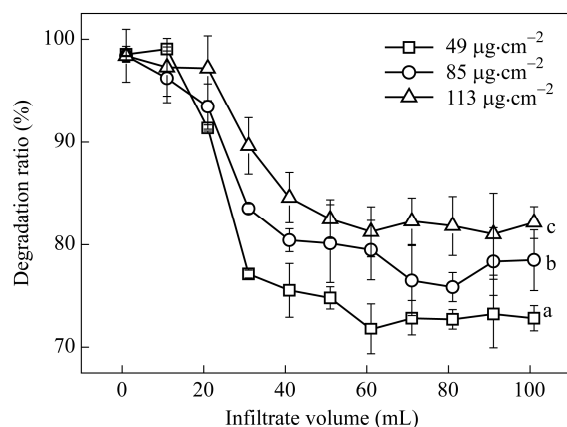


Fig. 8 Degradation ratio of methylene blue by the Au-PP membranes with polymerized dopamine contents of (a) $49 \mu\text{g}\cdot\text{cm}^{-2}$; (b) $85 \mu\text{g}\cdot\text{cm}^{-2}$; (c) $113 \mu\text{g}\cdot\text{cm}^{-2}$

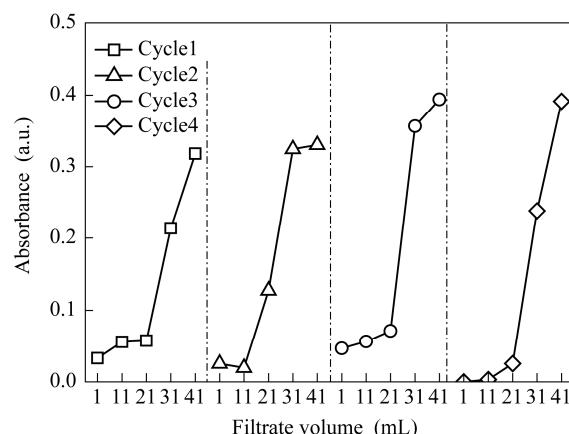


Fig. 9 The cycle performance of Au-functionalized membrane with four cycles

CONCLUSIONS

In summary, mussel-inspired adherence of dopamine was used to modify PP membranes to endow their surface with primary amines. Then, the primary amines were used to reduce chloroauric acid and obtain modified Au-PP membranes with Au nanoparticles having catalytic activity. The surface morphology and composition of membranes were characterized with SEM, FTIR and XPS, which demonstrated that the PP membranes were successfully modified by polymerized dopamine and Au nanoparticles. The catalytic performance of the functionalized Au-PP membrane was evaluated by the degradation of a methylene blue solution. Our results showed that the modified Au-PP membranes had excellent catalytic properties. As the catalytic efficiency decreased, the membranes could be regenerated by rinsing. However, the loading amount of Au nanoparticles and flux were still low. Therefore, further work should be done to improve the properties of the membrane.

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