A Performance-enhanced Electroosmotic Pump with Track-etched Polycarbonate Membrane by Allylhydridopolycarbosilane Coating

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Nanochannel plastic membranes are excellent materials for electroosmotic pump (EOP) elements owing to their surface charge properties, flexibility and cost-effectiveness. However, the surface charge properties of plastics are inferior to those of silicate-based materials. This paper reports a performance-enhanced EOP equipped with a glassified track-etch polycarbonate membrane (PC), which has a nanochannel surface covered by allylhydridopolycarbosilane (AHPCS). The effects of applied voltage, pH and membrane pore size on the electroosmotic flow velocity, along with a comparative study of the EOP with coated and pure membranes were investigated. It was found that when low DC voltage (10 – 40 V) was applied to both ends of the pump, the magnitude of the electroosmotic flow was linearly proportional to the voltage when the pore size of the membrane was less than 600 nm. A higher flow rate was obtained with larger pore size membranes. Compared with the uncoated film, the coated one showed faster electroosmosis velocity, with higher stability under the same conditions. For pH 10.0 buffer solution, a flow rate of 89.13 $\mu\text{L}/\text{min}$ was obtained in the modified membrane-based EOP with excellent repeatability and durability, while the flow rate was only 37.89 $\mu\text{L}/\text{min}$ in the bare PC membrane under 20 V. In order to demonstrate the performance of the developed EOP, the EOP was used for microcomplexometric titration to determine actual tap water hardness. The measured results were highly consistent with the results of a conventional complexometric titration method. The EOP with an AHPCS-coated plastic membrane expanded the application range to harsh condition solutions, such as high-concentration acids or bases.

Keywords Allylhydridopolycarbosilane, track-etched polycarbonate membrane, electroosmotic pump

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Introduction

Micropumps play a key role in manipulating the small volumes of sample and reagent required in biomedical, biological and environmental applications. As a non-mechanical micropump, an electroosmotic pump (EOP) is based on a fundamental electrokinetic phenomenon. Moreover, it has the characteristics of continuously and accurately transporting micro-liter and nano-liter fluids, no moving parts, no pulsation, no mechanical wear and avoiding micro-leakage from valves and conveying processes. EOP has been applied in flow injection analysis (FIA),¹ micro-, nano liquid chromatography (HPLC) separation,²⁻⁴ femto-pipette,^{5,6} electroosmotic droplet switch^{7,8} and micro-cooling systems.⁹

EOPs include open-channel, porous medium and membrane EOP, and the type differ in terms of the pump body and structural characteristics. Among them, track-etched nanochannel plastic membrane (polyethylene terephthalate (PET), polycarbonate (PC) and polyimide (PI)) based EOPs¹⁰⁻¹³ have attracted much attention owing to their characteristics for providing a high density of homogeneous short channels as well as excellent acid and alkali resistance. However, these membranes commonly have weak stability and durability of electroosmotic flow (EOF).

Another problem associated with conventional EOPs is the need for a high voltage supply (ranging from several hundred volts to several thousand volts), which increases the cost of the EOP. The surface electric property is the key factor that influences the outcome of their applications. Hence, modifying the surface properties of track-etched nanochannels is of great interest as the performance of nanodevices could be significantly improved. Physical adsorption methods such as using surfactants or ionic polymers are one of the approaches for modifying the surface charge property of nanochannels.^{7,14} Currently, chemical surface modification methods are also being utilized to change the surface charge density of track-etched nanochannels by amino-terminated chemicals and carboxylate-terminated species, or silica and titania forming reagents.¹⁵⁻¹⁷ However, these chemical modification processes are complicated and usually need many steps.

In our recent work, we reported a nanocoating method for coating the polydimethylsiloxane channel surface with preceramic polymer allylhydridopolycarbosilane (AHPCS, $-\text{[(allyl)SiH}_2\text{-CH}_2\text{]}_n$, Malta, NY, USA), and achieved durable electrokinetic performance with good chemical and thermal stability through silicate phase conversion.^{17,18} The active groups of silicon hydride (Si-H) in the polymer can be easily converted to silanol (Si-OH) species through alkaline hydrolysis.¹⁷ This coating method is also suitable for the modification of plastic-based micro-nanochannel surfaces.

In order to achieve a compact design and efficient operation,

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we designed an EOP with a glassified nanochannel polycarbonate (PC) membrane by AHPCS nanochannel coating. Factors¹⁹ affecting the performance of the EOP will be discussed with comparison to that with a pure PC membrane.

Experimental

Materials

Allylhydridopolycarbosilane (AHPCS, SMP10) was purchased from Starfire Systems Inc. (Malta, NY, USA). Track-etched nanochannel PC membranes (purchased from GVS, Life Sciences, USA) had a 1-inch diameter, working diameter of 7.5 mm defined by the O-ring used, and 60- μm thickness with nominal channel sizes of 200, 400 and 600 nm. Normal heptane, tetrahydrofuran (THF), boric acid, citric acid and trisodium phosphate were purchased from Aladdin (Shanghai, China). All chemicals were of analytical grade unless otherwise stated.

PC membrane modification

The process of surface modification includes three steps: coating, curing and hydrolysis. The AHPCS stock solution was prepared by weighing a certain amount of AHPCS, adding 1-wt% thermal initiator (dicumyl peroxide, Aldrich) and 2-wt% photo-initiator (Irgacure369, Ciba Specialty Chemicals Inc), which was diluted to become a 1-wt% polymer solution with normal heptane for nanochannel coating. Before coating the glossy and matte surface of the PC membranes, they were discharged for 30 s using a BD-20 (ETP, USA) corona processor, then those treated films were placed on a suction filter. To prevent nano-channel blockage during the coating process, the channel coating was carried out under vacuum pumping with ultraviolet (360 nm/5 W) consolidation for 10 min. Then, the films were thermally cured under 150°C for 2 h immediately after being taken out. After that, the membranes were soaked in 0.1 mol L⁻¹ NaOH solution, then hydrolyzed for 20 min, finally rinsed with distilled water.

Experimental setup

A schematic diagram of the entire setup is shown in Fig. 1. The setup consists of a 1-inch syringe filter holder, which was assembled on a surface modified PC membrane perpendicular to the flow direction, a pair of ϕ 0.3-mm Pt wires inserted into one side of the sealed polypropylene hollow fibers, and a low voltage DC power supply (MS1201D, Changzhou, China).

Results and Discussion

Figure 2 shows the scanning electron microscopy (SEM) images of the pure and AHPCS-coated PC membranes. The nanochannels obtained were roughly cylindrical with no crack formation. The average pore diameter was 174 nm (RSD 1.6%) and 162 nm (RSD 1.9%) for the pure and coated membrane, respectively. Measured volume capacities of three membranes by gravimetric method were 3.84×10^{-4} , 6.26×10^{-4} and $6.96 \times 10^{-4} \text{ cm}^3$ for 200, 400 and 600 nm, respectively. The capacity increases with increasing nominal nanochannel size. To further verify the coating, EDS analysis was conducted for both the coated and the bare membranes. Si elements were found in the EDS analysis of the coated film (Fig. 3). In our previous experiments, after the above series of treatments, the glassified surface provided an EOF of $4.9 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ at pH 8.0 with 2.0% RSD. The EOF was measured once every week for 3 months.¹⁷

The following describes the main factors that affect the performance of the EOP. To investigate the effect of the applied

Fig. 1 Schematic diagram A) and photo images of the EOP experimental system B). 1, DC power supply; 2, a pair of Pt wires; 3, nanochannel-coated PC membrane; 4, 1 inch syringe filter holder; 5, ϕ 0.5-mm polypropylene hollow fiber; 6, silicon tubings; 7 and 8, 100-mL glass beaker and conical flask; 9 and 10, stirrer and PTFE coated stirring bar.

Fig. 2 SEM images of 200-nm track etched PC membranes with pure PC membrane (A), and AHPCS-coated PC membrane (B).

Fig. 3 EDS analysis of the uncoated PC membrane (A), and coated PC membrane (B).

Fig. 4 Effect of voltage on the flow rate of the EOP.

external voltage to the flow rates of the EOP, an equivalent volume of universal buffer solution was injected into glass bottles on both sides of the AHPCS coated membrane. First, we marked the mass m_1 of the empty conical flask on one side after the liquid was discharged, and we marked the mass of the conical flask and the liquid m_2 , hence, $(m_2 - m_1)$ is the mass of the outflow liquid. Thus, the flow velocity v was calculated from the outflow time. The result is shown in Fig. 4.

An AHPCS-coated PC membrane was used with a channel size of 600 nm, and the voltage across the pump was adjusted to 10, 20, 30 and 40 V. The buffer solutions (pH 10.0) were composed of 0.2 mol/L boric acid, 0.05 mol/L citric acid and 0.1 mol/L trisodium phosphate²⁰ (the following buffer solution was the same). In general, the flow rate and output pressure of the EOP were positively correlated with the applied electric field. At low voltages of 2–6 V, the EOP also works well

except for the lower slope, while slope is larger at higher voltage ranges. When the applied voltage is above 60 V at pH 9, the current is up to 30 mA, and resulted in a variation of the EOF in our EOP system. Joule heat from high voltage elevates the solution temperature, and influences the EOF.^{21,22} The generation of bubbles will lead to the decrease of liquid flow rate at high voltage applications.²³ Bubbles caused by electrolysis of external electrodes will seriously affect the stability of the EOP system, resulting in current changes even power failure, thus leading to the inability to control the flow rate of the EOF. At present, this problem has been overcome by changing device components or changing micro-nano channel media. Here, both positive and negative electrodes were isolated with a pair of polypropylene hollow fibers in order to lead the produced gas out. This step offers a good solution to the gas problem up to 60 V in this system.

To study the effect of the membrane channel sizes on flow rate of the EOP, AHPCS coating and curing/hydrolysis were carried out with channel sizes of 200, 400 and 600 nm PC membranes (Fig. 5) under the buffer condition is the same as in Fig. 4. Figure 5 shows that when other conditions remain constant, the larger the pore size, the higher the flow rate, and the flow rate with the 600 nm channel size membrane is the highest. According to porosity data of the three membranes, porosity only slightly increases with the increase in pore size. This means that the increase in charge density with larger pores is not significant. Thus, the main reason for the increase in flow rate is simply the larger pore size.²⁴

Figure 6 shows the pH effect on flow rate of the EOP with the polymer coated and uncoated PC membrane. Using 600 nm pore size of AHPCS-treated and untreated membranes, and with the DC voltage fixed to 20 V, the flow rates with the coated films were significantly higher than that of the uncoated films. Moreover, the flow rates also increased with the increase of pH of the buffer solutions. Particularly, when pH > 7.0, the flow

Fig. 5 Effects of membrane channel size on the flow rate of the EOP.

Fig. 6 Effects of pH on the flow rate of the EOP.

rate of the coated membranes shows a significant upward trend. Because the degree of Si-OH deprotonation on the surface of AHPCS increases with the increase of pH, it causes increasing the ζ -potential of the channel surfaces to increase, and this results in higher flow rates.^{17,25}

To investigate the effect of water electrolysis on the EOP performance, a none-buffered KCl solution was selected as the working electrolyte. For the KCl solution with an ionic strength of 10 mmol/L, the flow rate was 5.68 $\mu\text{L}/\text{min}$, and ΔpH of the outlet fluid was 1.4 under 20 V working for 5 min. For the low ionic strength KCl (1 mmol/L) solution, the flow rate decreased to 0.64 $\mu\text{L}/\text{min}$ with the pH variation of 0.3 under the same experimental conditions. This explains that a buffer solution is necessary to keep a stable flow rate.

Reproducibility of the EOP in terms of flow rate is an important issue for practical use, but studies have not looked closely at this factor. Actually, the reliability of the EOP with bare plastic membrane has not yet been confirmed. The average relative standard deviation (RSD) value of flow rates of the EOP with AHPCS-coated PC membrane (600 nm) was 0.6% after three days running with pH 10.0 phosphate buffer. In our study of the long-term performance, the flow rates remained at 88.52 $\mu\text{L}/\text{min}$ with 2.3% RSD when measured twice every day for 1 week, while it fell slowly to 60–80% values depending on film batches for the bare PC-based EOP over the same period. The excellent reproducibility and durability of the EOP is

Table 1 Hardness determination of tap water by EOP complexometric microtitrations with a 600-nm PC membrane^a

	Conventional method			Proposed EOP method		
	1st	2nd	3rd	1st	2nd	3rd
V_{sample} , mL		100.00			5.00	
V_{EDTA} , mL	27.68	27.70	27.80	1.390	1.387	1.391
Hardness/ mg L^{-1}	277.60	277.80	278.81	278.81	278.20	279.01
Average/ mg L^{-1}		278.07			278.67	
RSD, %		0.18			0.11	

a. The concentration of EDTA standard solution is 0.01002 mol/L.

probably attributed to a fresh AHPCS interface formation through the Si-H hydrolysis in the solutions.¹⁷

HCl and NaOH solutions are widely used in chemical analysis. In an experiment to determine cyanide by pervaporation-flow injection analysis, both NaOH and HCl solutions must be delivered by pumps.²⁶ To realize a miniaturized analytical system, a plastic membrane based EOP is the preferred consideration. To study the applicability of the EOP under strong acid or alkali solutions, the EOP flow rates were measured for 0.1 mol/L NaOH and HCl solution with 600 nm pore size membrane at 10 V, and they were +38.12 and −13.68 $\mu\text{L}/\text{min}$, respectively. It is worth noting that the EOP keeps working even when the concentration of HCl and NaOH increased to 4.0 mol/L. In both cases, the surface coating of the PC film showed no obvious change in appearance. However, serious corrosion of the positive platinum electrode was found. This acid-alkali resistive property of the EOP with AHPCS-coated PC membrane shows considerable superiority compared to an EOP with porous anodic alumina oxide (AAO) membrane, which easily dissolves in acids and bases without surface protection.²⁷

A micro-complexometric titration was conducted using the developed EOP to determine the hardness of tap water. The measured results are listed in Table 1.

The conventional complexometric titration process is as follows: place 100.00 mL of tap water sample into a 250-mL conical flask, add 5 mL $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution (2 g NH_4Cl + 10 mL $\text{NH}_3\cdot\text{H}_2\text{O}$ diluted to 100.00 mL), and 2–3 drops of 5.0 g L^{-1} Eriochrome Black T indicator solution, and then titrate, and calculate the total hardness of the water sample. The EOP microtitration allows for a reduction in the sample volume to 5.00 mL of tap water. The sample is placed in a 50-mL conical flask, to which 0.25 mL $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution is added, and 1 drop of Eriochrome Black T indicator solution, then placed on a magnetic stirrer and switched on. Then, the total hardness of the water sample was calculated by titrating with EDTA (0.01 mol L^{-1}) standard solution until the color of the solution just changes from red to blue. The value of total hardness represented by $\text{mg}(\text{CaCO}_3) \text{L}^{-1}$ was expressed by $c_{\text{EDTA}}M_{\text{CaCO}_3}/V$, where c is the concentration of EDTA, V_{EDTA} is the EDTA volume consumed, M_{CaCO_3} is the relative molecular mass of CaCO_3 , and V is the volume of tap water sample. The measurement was repeated 3 times in parallel to obtain the average value of total hardness of the tap water.

As can be seen from Table 1, the average water hardness measured by conventional and EOP micro-titration methods are 278.07 and 278.67 mg/L, respectively. The national standard for drinking water in China is ≤ 450 mg/L. Compared with the standard hardness of water stipulated by the state, the total hardness of water measured in the experiment is within the

normal range. In addition, the experimental results of the micro-titration and conventional titration are reliable with no significant difference. The relative average deviations of both experiments are in line with the requirements of titration analysis. Moreover, the EOP micro-titration could reduce reagent consumption as well as subjective experimental error in titration experiments.

Conclusions

In summary, a novel, simple and low-cost EOP with AHPCS surface modified PC membrane is demonstrated. Compared with that of bare PC film, the coated one shows faster electroosmosis velocity, stronger controllability and higher stability under the same conditions. The acid-base and organic solvent resistive properties will expand its application range to harsh chemical conditions, and also help to solve the limitations of low flow rates of other plastic membrane-based EOPs.

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