A performance-enhanced electroosmotic pump with track-etched polycarbonate membrane by allylhydridopolycarbosilane coating

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Abstract

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 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 at both ends of the pump, the magnitude of the electroosmotic flow was linearly proportional to the voltage when the pore sizes of membrane were below 600-nm. Higher the flow rate obtained with larger pore size membrane. 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 μL/min obtained in the modified membrane based EOP with excellent repeatability and durability, while the flow rate was only 37.89 μL/min in the bare PC membrane under 20 V. In order to demonstrate the performance of the developed EOP, the EOP was used to a microcomplexometric titration to determine actual tap water hardness. The measured results were considerably consistent with a conventional complexometric titration. The EOP with an AHPCS-coated plastic membrane expanded the application ranges to harsh condition solutions like high concentration acids or bases.

Keywords: Allylhydridopolycarbosilane; track-etched polycarbonate membrane; electroosmotic pump.
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, 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 process. EOP has been applied in flow injection analysis (FIA)\textsuperscript{1}, micro-, nano liquid chromatography (HPLC) separation\textsuperscript{2-4}, femto-pipette\textsuperscript{5,6}, electroosmotic droplet switch\textsuperscript{7,8} and micro-cooling systems\textsuperscript{9}.

EOP covers open channel, porous medium and membrane EOP according to the difference between the pump body and its structural characteristics. Among them, track-etched nanochannel plastic membrane (polyethylene terephthalate (PET), polycarbonate (PC) and polyimide (PI) ) based EOP\textsuperscript{10-13} has attracted much attention owing to providing a homogeneous and high density of 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 accompanied with conventional EOP is the need of a high supplied voltage (ranging from several hundred volts to several thousand volts), which increase cost of EOP. The surface electric property is the key ingredient that influences the outcomes 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 to modify the surface charge property of nanochannels\textsuperscript{7,14}. Currently, chemical surface modification methods have also been 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\textsuperscript{15-17}. However, these chemical modification processes are complicate and usually need many steps.
In our recent work, we reported a nanocoating method on polydimethylsiloxane channel surface with preceramic polymer allylhydridopolycarbosilane (AHPCS, -(allyl)SiH2–CH2)-, Malta, NY, USA), and achieved durable electrokinetic performances with good chemical and thermal stability through silicate phase conversion. The active groups of silicon hydride (Si–H) in the polymer can be easily converted to silanol (Si–OH) species through alkaline hydrolysis. This coating method is also suitable for the modification of plastic-based micro-, nanochannels.

In order to achieve compact design and efficient operation, we designed an EOP with a glassified nanochannel polycarbonate (PC) membrane by AHPCS nanochannel coating. Factors affecting the performance of the EOP will discuss with comparison to that with 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) are of 1 inch diameter, working diameter of 7.5 mm defined by used O-ring, and 60-μm thickness with nominal channel sizes of 200-nm, 400-nm and 600-nm, respectively. 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 microfluidic channel coating. Before coating the glossy and matte surface of the PC membranes, they are discharged for 30 s using a BD-20 (ETP, USA) corona processor, then those treated films are placed on a suction filter. To prevent the nano-channel blockage during coating process, the channel coatings are proceeded under vacuum pumping with ultraviolet (360 nm/5 W) consolidation for 10 min. Then, thermally cured under 150°C for 2 hr immediately after the films are taken out. After that, the membranes are soaked in 0.1 mol L⁻¹ NaOH solution, hydrolyzed for 20 min, then final 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

Fig. 2 is the scanning electron microscopy (SEM) images of the pure and AHPCS-coated PC membranes. The resulted nanochannels are roughly cylindrical with no crack formation. The average pore diameter was 174 nm (RSD 1.6%) and 162 nm (RSD 1.9%) with the coated and pure membrane, respectively. Measured volume capacities of three membranes by gravimetric method were $3.84 \times 10^{-4}$ cm³, $6.26 \times 10^{-4}$ cm³ and $6.96 \times 10^{-4}$ cm³ for 200-nm, 400-nm and 600-nm, respectively. The capacity increases with increasing nominal nanochannel size. To further confirmation of the coating, EDS analysis were conducted to both the coated and the bare membranes. The Si elements was found in the EDS analysis from the coated film (Fig.3). In our previous experiments, after the above series treatments, the glassified surface provides an EOF of $4.9 \times 10^{-4}$ cm² /V·s at pH 8.0 with 2.0% RSD. The EOF is measured once every week for 3 months.¹⁷
Following description is the main factors that affect the performance of EOP. To investigate the effect of the applied external voltage to the flow rates of EOP, equivalent volume of universal buffer solutions was injected into glass bottles on both sides of the AHPCS coated membrane. First, mark the mass $m_1$ of the empty conical flask on one side, after the liquid is discharged, mark the mass of the conical flask and the liquid is $m_2$, hence, $(m_2-m_1)$ is the mass of the outflow liquid. Thus, the flow velocity $\nu$ is calculated with the outflow time. The result is shown in Fig.4.

AHPCS-coated PC membrane was used with a channel size of 600-nm, the voltage across the pump was adjusted to 10, 20, 30, 40 V, respectively. 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 phosphate\textsuperscript{20} (the following buffer solution is the same). In general, the flow rate and output pressure of the EOP are positively correlated with the applied electric field. At low voltages of 2-6 V, the EOP also works well except for the lower slope, as slope is large at higher voltage ranges. When the applied voltage is above 60 V at a pH 9, the current is up to 30 mA, and resulted in variation of the EOF in our EOP system. Joule heat from high voltage elevates solution temperature, and influences on the EOF\textsuperscript{21,22}. The generation of bubbles will lead to the decrease of liquid flow rate at high voltage application\textsuperscript{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 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) and the buffer condition is same with in Fig. 4. Figure 5 shows when other conditions remain constantly, the larger pore size is, the larger flow rate is, and the flow rate with 600-nm channel size of membrane is the largest. According to porosity data of three membranes, porosity only slightly increases with the increasing in pore size. This means that the increase in charge density with larger pore is not significant. Thus, the main reason of the increase in flow rate is simply resulted from the increase of pore size\textsuperscript{24}.

Figure 6 is pH effect on flow rate of the EOP with the polymer coated and uncoated PC membrane. Using a 600-nm pore size of AHPCS-treated and untreated membrane, and fixed DC voltage to 20 V. The flow rates with coated films are significantly higher than that of uncoated. Moreover, the flow rates also increased with the increase of pH of the buffer solutions. Particularly, when pH>7.0, the flow rate of the coated membranes presents a significant upward trend. This is because of the degree of Si-OH deprotonation on the surface of AHPCS increases with the increase of pH, then causes the ζ-potential of the channel surfaces increase, and resulting higher flow rates\textsuperscript{17,25}.

To investigate the effect of water electrolysis on the EOP performance, a none-buffered KCl solution selected as the working electrolyte. For the KCl solution with an ionic strength of 10 mmol/L the flow rate is 5.68 μL/min, and ΔpH of outlet fluid is 1.4 under 20 V working for 5 min. For the low ionic strength of KCl (1 mmol/L) solution the flow rate decreased to 0.64 μL/min with the pH variation of 0.3 under the same experimental conditions. This explains 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 most literatures has not involved. Actually, the EOP with bare plastic membrane has not yet achieved the reliability. 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 the long-term performance, the flow rates remained at 88.52 μL/min.
with 2.3% RSD when measured twice every day for 1 week, while it is falling slowly to 60~80% values depending on film batches with same period in the bare PC-based EOP. The excellent reproducibility and durability of the EOP is probably from a fresh AHPCS interface formation through the Si-H hydrolysis in the solutions\textsuperscript{17}.

HCl and NaOH solutions are widely used in chemical analysis. In an experiment of determining cyanide by pervaporation-flow injection analysis, both NaOH and HCl solutions are need to deliver by pumps\textsuperscript{26}. To realize miniaturized analytical system, 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 of were measured for 0.1 mol/L NaOH and HCl solution with 600-nm pore size membrane at 10 V, and they are +38.12 and -13.68 μL/min respectively. It is worth noting that the EOP keeps working even the concentration of HCl and NaOH increased to 4.0 mol/L by further investigation. In both cases, the surface coating of the PC film has no obvious change in appearance. However, serious corrosion of the positive platinum electrode was found. This acid-alkali resistive properties of the EOP with AHPCS-coated PC membrane shows much superiorities compared to EOP with porous anodic alumina oxide (AAO) membrane which easily dissolves in acids and bases without surface protection\textsuperscript{27}.

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

The process of conventional complexometric titrations are follows: remove 100.00 mL of tap water sample into 250 mL conical flask, add 5 mL NH\textsubscript{3}-NH\textsubscript{4}Cl buffer solution (2 g NH\textsubscript{4}Cl + 10 mL NH\textsubscript{3}·H\textsubscript{2}O diluted to 100.00 mL), and 2~3 drops of 5.0 g·L\textsuperscript{-1} Eriochrome Black T indicator solution, and then titrate, calculate the total hardness of water sample. The EOP microtitrations reduce the sample volume, 5.00 mL of tap water is placed in a 50 mL conical flask, add 0.25 mL NH\textsubscript{3}-NH\textsubscript{4}Cl buffer solution, and 1 drop of Eriochrome Black T indicator
solution, and switched on magnetic stirrer. Then, titrate with EDTA (0.01 mol·L⁻¹) standard solution until the solution just changes from red to blue, measure it for 3 times in parallel, calculate the total hardness of water sample, and the result is represented by \( x \text{ mg(CaCO}_3\text{)} \cdot \text{L}^{-1} \). The calculation formula is:

\[
\text{Total hardness} = c \cdot V_{\text{EDTA}} \cdot M_{\text{CaCO}_3} / V
\]

Where \( c \) is the concentration of EDTA, \( V_{\text{EDTA}} \) is the EDTA volume consumed, \( M_{\text{CaCO}_3} \) is the relative molecular mass of \( \text{CaCO}_3 \), \( V \) is the volume of tap water sample.

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 \( \leq 450 \text{ mg/L} \). 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 reagents 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 enable to solve the limitations of low flow rates of other plastic membrane-based EOP.

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

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

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

Fig. 1  Schematic diagram A) and photo images of the EOP experimental system B).

1: DC power supply; 2: a pair of Pt wire; 3: nanochannel coated PC membrane; 4: 1-Inch syringe filter holder; 5: φ 0.5-mm polypropylene hollow fiber; 6: silicon tubings; 7,8: 100-mL glass beaker and conical flask; 9,10: stirrer and PTFE coated stirring bar.

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

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

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

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