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# Layer-by-layer self-assembly of polyelectrolyte complexes and their multilayer films for pervaporation dehydration of isopropanol

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## ABSTRACT

Two negatively charged polyelectrolyte complex colloidal nanoparticles ($PEC^-$) and one positively charged nanoparticle ($PEC^+$) were prepared and used as novel layer-by-layer (LbL) building blocks. These PEC nanoparticles include poly(2-methacryloyloxy ethyl trimethylammonium chloride)/sodium carboxymethyl cellulose (PDMC/CMCNa $PEC^-$), poly(diallyldimethylammonium chloride)/CMCNa (PDDA/CMCNa $PEC^-$) and PDDA/poly(sodium-*p*-styrenesulfonate) (PDDA/PSS $PEC^+$). LbL multilayer films based on ($PEC^+/PEC^-$) were constructed on both quartz slides and modified polyamide (MPA) reverse osmosis support membranes. UV–vis spectroscopy, quartz crystal microbalance (QCM), field emission scanning microscopy (FESEM) and atomic force microscopy (AFM) were utilized to follow the thickness growth and morphology evolution of these multilayer films with increasing bi-layer numbers. LbL multilayer films deposited on MPA support membranes were subjected to pervaporation dehydration of 10 wt% water–isopropanol and effect of bi-layer numbers and feed temperature on pervaporation performance was studied. Generally, $PEC^+/PEC^-$ can be LbL self-assembled successfully on both substrates with a thickness growth rate ca. 200 nm/bi-layer. Moreover, $PEC^+/PEC^-$ multilayer films show high pervaporation performance with film thickness up to several micrometers. For example, performance of the multilayer films in dehydrating 10 wt% water–isopropanol at 50 °C is $J = 1.18\ \mathrm{kg/m^2\,h}$, $\alpha = 1013$ for $(PEC^+/\text{PDMC-CMCNa } PEC^-)_{24}$ and $J = 1.36\ \mathrm{kg/m^2\,h}$, $\alpha = 938$ for $(PEC^+/\text{PDMC-CMCNa } PEC^-)_{25}$, respectively.

## 1. Introduction

Pervaporation (PV) is a widely studied membrane separation technique which is particularly advantageous in separating azeotropes [1–6]. Feed molecules pass through a membrane under PV operation mainly via sorption–diffusion model [7] and the physiochemical properties of membrane materials play a dominant role in determining their performance. Thus, one central target of PV research is to develop novel membrane materials or membrane fabrication method, aiming to achieve the most advanced performances. Layer-by-layer (LbL) self-assembly is a technique developed recently for building up multilayer films with controlled thicknesses in nano-scale [8]. LbL was adopted by membranologists to fabricate ultra-thin films for PV soon after its invention. Tieke et al. first made a multilayer film between poly(allylaminehydrochloride) and poly(styrene sulfonate sodium salt) (PAH/PSS) on polyacrylonitrile support membrane and utilized it in ethanol dehydration [9,10]. Following this attempt, they further found that multilayer films based on high charge density polyelectrolyte such as polyethyleneimine (PEI) and polyvinylsulfate (PVS) show much higher selectivity [11–14]. Meanwhile, effect of polyelectrolyte types, LbL building up conditions and post-treatment on the PV performance have also been studied independently by other groups [15–20]. These studies build up a fundamental understanding about using LbL multilayer films in PV dehydration. Then, research interest begun to focus on how to speed up the LbL building up process so that multilayer films can be constructed more efficiently. Feng et al. optimized the building up conditions to achieve high PV performance with less bi-layer depositions [19,20]. Zhang et al. proposed dynamic and electric field LbL method for speeding up LbL process and applied this method to both planar substrate [21–23] and hollow fiber [24,25]. Our group also proposed an electric field enhanced LbL technique for speeding up the LbL process [26,27].

However, it is noticed that some fundamental questions remain open in the interdisciplinary field of LbL self-assembly and PV. For example, the building blocks of LbL multilayer films that used in PV are restricted to common polyelectrolyte till now [9–27]. This restriction seems somewhat surprising because the LbL technique

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is readily available to various species such as colloidal particles, micelles, inorganic particles and so on [28]. Moreover, thicknesses of multilayer films that used in PV are usually limited to tens or hundreds of nanometers. Thus, it becomes arguable whether the commonly observed high flux of LbL multilayer films in PV dehydration will be reduced with increasing the film thickness to several micrometers. In addition, it is also not very clear whether the high flux of LbL multilayer films is due to their ultra-low film thicknesses or their unique ionic cross-linking and layered structures. In this study, we use charged polyelectrolyte complex (PEC) colloidal aggregates as novel LbL building blocks to prepare LbL multilayer films for PV dehydration. Our aim is to deal with the questions mentioned above. PEC particles are chosen as LbL building blocks due to their unique structural characteristics. Firstly, PEC particles have large sizes in solutions up to ca. 100 nm, making it possible to construct a micrometers thick multilayer film from them within less bi-layer numbers. Note that such speeding up is achieved without changing the external LbL building up conditions. Secondly, the structure of PECs is inherently identical with that of LbL multilayer film because both are ionic cross-linked [29]. Thus, using PEC particles as LbL building blocks reserves the typical ionic cross-linking structure of traditional LbL multilayer films. The last reason is that our previous results show that PEC casting membranes show ultra-high performances in PV dehydration [30–33].

## 2. Experimental

### 2.1. Materials

Sodium carboxymethyl cellulose (CMCNa, degree of substitution: 0.85) was purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Its intrinsic viscosity in 0.01 M NaCl at 30 °C is 1198.3 mL/g. Poly(2-methacryloyloxy ethyl trimethylammonium chloride) (PDMC, *M*w = 300 000 g/mol) was obtained from HenYi chemical plant (Shanghai, China). Poly(diallyldimethylammonium chloride) (PDDA, *M*w = 100 000–200 000 g/mol, 20% aqueous solution) and poly(sodium-*p*-styrenesulfonate) (PSSNa, *M*w = 70 000 g/mol) were purchased from Aldrich. Modified polyamide reverse osmosis membrane (MPA) (polysulphone/polyethylene terephthalate was used as supported membrane and the polyamide surface was modified with acryl chloride) with negative charges was used as substrate [26,27]. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were analytical reagents. Deionized water with a resistance of 18 MΩ cm was used in all experiments.

### 2.2. Preparation of negatively and positively charged PEC nanoparticles

Two types of negatively charged PEC nanoparticles (PDMC/CMCNa PEC$^-$ and PDDA/CMCNa PEC$^-$) and one type of positively charged PEC nanoparticles (PDDA-PSSNa PEC$^+$) were prepared. PEC$^-$ colloidal nanoparticles were prepared according to our previous method [30,31]. CMCNa solution (monomer mole unite concentration: 0.01 M) was mixed with PDMC solution (0.01 M) in 0.009 M HCl. PDMC/CMCNa PEC solids were obtained after reaching the endpoint of ionic complexation between PDMC and CMCNa. Then, PDMC/CMCNa PEC solid was dissolved in NaOH to obtain a PEC$^-$ aqueous solution (0.1 wt%). The PDDA/CMCNa PEC$^-$ was prepared in the same way as that of PDMC/CMCNa PEC$^-$. PDDA-PSS PEC$^+$ was prepared according to nonstoichiometric mixing method [34]. PSS (0.036 g) was added into 100 mL of 0.1 wt% PDDA solution under vigorous stirring. Turbidity occurred upon mixing and no precipitate appeared. All these aqueous PEC solutions were stable in a month and freshly prepared PEC$^+$ particles were used for LbL assembly. The monomer mole ratio of PDMC to CMCNa for PDMC/CMCNa PEC$^-$ is 0.3 and monomer mole ratio of PDDA to CMCNa for PDDA/CMCNa PEC$^-$ is 0.19 according to elemental analysis. Fig. 1 shows the chemical structures of the three PEC nanoparticles and it is seen that the negative charge of PEC$^-$ is due to the COONa groups and the positive charge of PEC$^+$ is due to the excessive PDDA.

### 2.3. Layer-by-Layer self-assembly

LbL self-assembly of oppositely charged PEC nanoparticles was carried out on AT-cut quartz crystals with gold electrode for measuring the thickness growth, on quartz slides (10 mm × 20 mm) for measuring the UV–vis absorption and on MPA support membrane for PV dehydration. AT-cut quartz crystals and quartz slides were cleaned by immersion in freshly prepared piranha solution (3:7 mixture of 30% $H_2O_2$ and concentrated $H_2SO_4$) for 30 min followed by thorough rinsing with deionized water and drying with nitrogen prior to use. (***Caution!*** *Piranha solution is a very strong oxidizing agent and reacts violently with organic compounds. It should be handled with extreme care.*) The concentrations of all PEC dipping solutions (salt free) are 0.1 wt% and their pH values are adjusted to 9. Substrates were subsequently dipped into PEC dipping solutions for 10 min, followed by rinsing with deionized water (pH 9) each layer (6 times, 20 s each time). Prior to the LbL deposition of PEC nanoparticles, three PDDA/PSS bi-layers (referred to as $(PDDA/PSS)_3$) were firstly deposited on the substrate to facilitate the adsorption of PEC nanoparticles. Note that the concentration of PDDA and PSS solutions for fabricating $(PDDA/PSS)_3$ was 0.2 wt% and 1 M NaCl was added.

### 2.4. Pervaporation

The pervaporation of LbL multilayer films was operated on a laboratory made apparatus reported previously [35]. Flux ($J$) and separation factor ($\alpha$) were calculated through following equations.

$$J = \frac{\Delta g}{S \times \Delta t}$$

$$\alpha = \frac{P_{H_2O}/P_{IP}}{F_{H_2O}/F_{IP}}$$

$\Delta g$ is the permeate weight collected during the operation time $\Delta t$ and $S$ is the membrane area (18.09 cm$^2$). $F_{H_2O}$ and $F_{IP}$ are the weight fractions of water and isopropanol in the feed and $P_{H_2O}$ and $P_{IP}$ are those in permeate, respectively. Data of PV performance were tested three times and averaged.

### 2.5. Characterizations

FT-IR spectra were obtained with a BRUKER VECTOR 22 FT-IR spectrometer. Element analysis was operated on Flash EA1112 (ThermoFinnigan, Italy). The UV absorptions spectra (200–400 nm) of multilayer films on quartz slides were measured using a Cary 100BIO UV–vis spectrometer. Clean bare quartz slide was a used as reference. Water contact angles (CA) were measured by sessile drop method using a contact angle meter (OCA 20, Dataphysics Instruments GmbH, Germany) at 25 °C and at about 65% relative humidity. The thickness growth of the LbL multilayer films was monitored by quartz crystal microbalance (QCM, Resonance Probe GmbH, Goslar, Germany). AT-cut quartz crystals (Maxtek) with a fundamental frequency, $f_0$, of 5 MHz and gold electrodes were used. The multilayer films were fabricated on the front side of the quartz crystal. The frequency shift of the quartz crystal, $\Delta f$, after the deposition of each layer was measured at third overtone order $n = 3$ (i.e.