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Hydrophobization of multilayered film containing layer-by-layer assembled nanoparticle by Nafion adsorption

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Summary

The multilayered film on a glass substrate, assembled from cationic poly(ethyleneimine) (PEI), anionic nano-sized polystyrene (PS) latex particle and cationic PEI or poly(allylamine hydrochloride) (PAH) layer was prepared by using the layer-by-layer (LbL) technique. Hydrophobization was carried out by immersing the film in Nafion solution. The hydrophobicity with high contact angle value was achieved by adjusting deposition ionic strength and ratio of water/ethanol of Nafion solution. The existence of PS particles in the LbL film significantly enhanced hydrophobicity of the film surface.

Introduction

Research on the so-called "lotus effect", which is due to innumerable fine projections coated with water-repellent wax on the leaf, has been widely extended to the extremely hydrophobic smooth solid surface bearing small wax particles for self-cleaning surface application [1-6]. For the preparation, the combination of surface roughness and low surface energy is required [3-7]. A surface with excellent hydrophobicity, i.e., with contact angle of water droplet larger than 150^o, could be obtained when a surface structure containing holes and pins vertical to the surface was coated with a hydrophobic chemical [4-6]. A fluoropolymer which provides good repellency towards both polar and apolar liquids, low surface tension and inert to chemical substances is one of the important hydrophobic coatings [8]. It is not surprising that Nafion, consisting of tetrafluoethylene (TFE) backbone and ether side chains terminated with the sulfonic group, in the solution form has been applied for casting into electrode-membrane assembly [9]. Previous studies showed that the property of Nafion, such as charge content, diffusion rate and morphology, was strongly influenced by the nature of solvent, water content and ionic strength [9,10]. However, the contact angle of PTFE film is not high enough for mimicking the lotus-like surface [11]. The need of Nafion coating and an additional hydrophobic behaviour should, therefore, be considered. The self-cleaning surface might be developed by depositing nanostructured hydrophobic particles onto the substrate surface [1,5,12]. The layer-by-layer (LbL) technique, an alternate immersion of substrate onto the oppositely charged polyelectrolyte solution, which is a powerful method of constructing ultrathin films with tailored structure [4,13-15], has been of great interest for exploration of particle deposition. Due to the fact that electrostatic attraction is the driving force for the multilayer build-up and the process is independent of the substrate size and topology [13,14], this approach allows fabrication of products that are normally difficult or impossible to conventionally produce. In addition, many different materials including light emitting and conducting polymers can be incorporated into the multilayered film and that the film architectures have thoroughly been determined.

We now wish to report the use of LbL technique in the preparation of multilayered film whose surface was then hydrophobized by Nafion adsorption. To provide the rough surface, the nano-sized monodisperse polystyrene (PS) latex particles were adsorbed onto a glass surface having a layer of cationic poly(ethyleneimine) (PEI). Due to the sulfonate head group of Nafion which cannot be directly adsorbed onto the multilayered film, having anionic PS particles as the top layer, the cationic polyelectrolyte, i.e., PEI or poly(allylamine hydrochloride) (PAH), was used as a binder between the two layers. Finally, the outermost layer of film was masked with Nafion to provide a hydrophobic top surface. The optimum conditions for providing hydrophobic surface of the multilayered film were examined by considering major factors, e.g., ionic strength and the ratio of ethanol to water in the mixed solvent of Nafion.

Experimental

Materials

Branched PEI (M_w = 750 000 g·mol^{-1}, BASF), PAH (M_w = 70 000 g·mol^{-1}, Aldrich), sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) (Merck) were used as received. Carboxylate PS latex, provided by Institut Charles Sadron (ICS, Strasbourg, France), was characterised by particle size and zeta potential determinations (Zetasizer 3000 HS, Malvern). This latex, having 215±1 nm in average particle diameter and -49.1±0.6 mV of zeta potential, was then cleaned by the serum replacement method [16,17]. The conductivity of serum or washed water was measured by a conductivity meter (Radiometer, CPM 83) until its conductivity was found to be similar to that of the ultrapure water (Milli-Q plus, Millipore) of 1-2 μScm^{-1}.

A Nafion solution was prepared by diluting 500 mg of commercial Nafion (5% in aliphatic alcohols/water solvent (Aldrich)) with 100 mL of ethanol (Merck):Milli-Q water in a ratio of 0:100, 15:85, 50:50, 75:25, 100:0.

Preparation of multilayered film

A glass slide was cleaned by immersing in the mixture of methanol and concentrated HCl (1:1) for 30 min followed by 30 min of dipping in concentrated H_2SO_4. The substrate was finally rinsed several times with Milli-Q water and then dried with N_2 flushing.

For LbL assembled film preparation, the dried substrate was dipped into an aqueous solution of PEI (3×10^{-3} monomolar based on repeating unit) for 30 min and then washed three times with Milli-Q water before drying with N_2. The positively charged substrate obtained was next immersed in the anionic PS latex with 5×10^{10} particles/cm^3, 5×10^{-5} M of sodium chloride (NaCl) (Merck) at pH 6. After washing and drying, the sample coated with particles was consecutively immersed for 30 and 20 min, respectively, in solutions of PEI and Nafion. In the case of PAH, the sample, before dipping into Nafion solution, was immersed in an aqueous solution of PAH (3×10^{-3} monomolar) for 20 min.

Surface coverage of latex particles

The multilayered film on a glass substrate was cut into a rectangular shape (1.0×1.0 cm^2) and then coated with gold, using a sputter coater (BEC-TEM), for 30 seconds before the study under a scanning electron microscope (SEM; Hitachi 2300S). The micrograph of the film was used to determine the surface coverage (Cs), the amount of colloidal particles adsorbed per unit area, as calculated from the following equation.

$$\mathrm{Cs}\,(\%) = \frac{N}{N_{\max}} \times 100$$

Where N and $N_{\max}$ are number of deposited particles and maximum number of particles per unit area respectively [18].

Contact angle measurement

The contact angle of a water droplet (5 μL) on the film surface was determined by using the standard sessile drop technique (Digidropmeter, GBX). A minimum of twenty separated locations on a specimen were measured and the average value of three specimens was reported.

Results and Discussion

Effect of cationic polyelectrolyte

The cationic polyelectrolyte, i.e., PEI or PAH, was used as the binder between Nafion molecules and the surface of anionic PS particles according to the conditions described above to provide the maximum surface coverage of PS particles on the PEI-coated glass substrate. The SEM micrograph obtained is presented in Figure 1 which indicated that the surface coverage (%Cs) of PS particles on a PEI-coated glass substrate was 45%.

The PEI or PAH (3×10^{-3} monomolar) was next generated as the third layer followed by the adsorption of Nafion (using ethanol to water, 85:15, in the absence of NaCl) as the outermost layer. The contact angle of the substrate after each deposition step was measured and the data are shown in Table 1.

From Table 1, the contact angles of 94°-100° of the multilayered film covered with Nafion indicated the role of its hydrophobic part at the top surface, i.e., sulfonic group

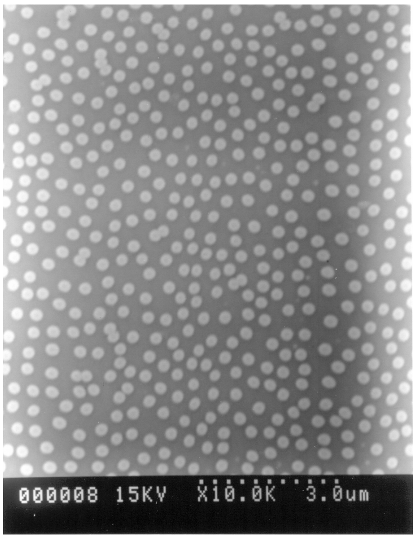

Figure 1. SEM micrograph of cleaned PS particles (5 × 10^{10} particles/cm^3) having NaCl (5 × 10^{-5} M) deposited on PEI-coated glass substrate at pH 6 for 30 min

Table 1. Contact angle of the outermost layer of glass substrate at each deposition step before final adsorption of Nafion (500 mg/100 mL of ethanol to water, 85:15, in the absence of NaCl and immersion time for 20 min)

Substrate	Contact angle (degrees)
Glass/PEI	33 ± 1
Glass/PEI/PS	24 ± 1
Glass/PEI/PS/PAH	46 ± 2
Glass/PEI/PS/PEI	33 ± 1
Glass/PEI/PS/PAH/Nafion	94 ± 1
Glass/PEI/PS/PEI/Nafion	100 ± 2

($-SO_3^-$) preferentially anchored the cationic chains (PEI or PAH) onto the film while the backbone of PTFE dangled out of the surface. It was also observed that the contact angle of the Nafion adsorbed on the PEI layer was higher than that adsorbed on PAH chains. This could be explained by considering chemical structure of both polyamines used [19,20]. It was reported that PAH, a linear polymer chain, would lay flatly on top of the mica substrate [19]. Presumably, some side chains of a branched PEI dangled much deeper into the solution [19] and, hence, would interact more with $-SO_3^-$ of Nafion to enhance the amount of adsorbed Nafion. Alternatively, this might come from the composition of the two polyamines, i.e., PEI composes of primary:

secondary: tertiary amine groups in a ratio of 35:38:27 [21] whereas PAH consists of only primary amine [19,20,22]. The amines in PEI would easily react with $–SO_3^-$ groups in Nafion to give corresponding ammonium salts $((R_2NH_2^+)(SO_3^-))$ and, as a result of this acid-base reaction, high amount of Nafion would be adsorbed. In contrast, the ammonium salts in PAH could only interact with $–SO_3H$ in Nafion via electrostatic interaction. The results of PEI leding to high amount of Nafion adsorbed on the substrate surface compared to that in the case of PAH agreed well with those reported in the former work in which the film having PEI as an intermediate layer between poly(tetrafluoroethylene-*co*-hexafluoropropylene) and poly(acrylic acid) (PAA) was more hydrophobic than that of the film using PAH [22].

Effect of ethanol/water mixed solvent of Nafion

Nafion dissolves well in the alcohol-water mixture [23] due to the fact that water interacts directly with the sulfonic acid group in Nafion while alcohol might be able to solvate the fluoroether rich region [24]. In addition, alcohol containing methyl ($-CH_3$) group could strongly interact with perfluorohydrocarbon skeleton via van der Waals interaction [23]. The contact angle of multilayered film after immersing into Nafion solution, using various ethanol to water ratios, in the absence of NaCl was, therefore, measured and the data obtained are shown in Figure 2.

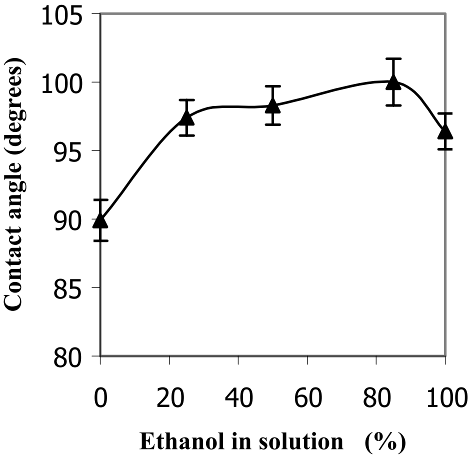

Figure 2. Effect of solvent ratios of ethanol to water in mixed solvent of Nafion (500 mg/100 mL, in the absence of NaCl and immersion time of 20 min) adsorbed on PEI layer (3×10^{-3} monomolar, immersion time of 30 min) deposited onto glass substrate roughened by PS particles

As shown in Figure 2, it was observed that the contact angle of the multilayered film dipping in an aqueous solution of Nafion (without ethanol) was about $90^o \pm 2^o$. With the increasing of ethanol content, the contact angle significantly increased until approaching the maximum value of 100° ± 1° when using 85% of ethanol. It might be explained that without ethanol, water interacted with sulfonic group of Nafion while perfluorohydrocarbon adopted a collapsed conformation [25]. On the other hand, ethanol could penetrate and plasticise Nafion molecules and, hence, increase in mobility of the fluorocarbon region [26,27]. The number of clusters of Nafion, therefore, increased while their size decreased [28]. Consequently, an increase in ethanol content in the mixed solvent enhanced the amount of Nafion contacted to the layer of PEI previously coated on the substrate. For the same reason, when 100% ethanol was used, the electrostatic attraction between polar part of Nafion molecules and that of PEI decreased. The amount of adsorbed Nafion on the outermost surface in the latter case lowered and, consequently, the film became less hydrophobic.

Effect of immersion time

The adsorption kinetics of polyelectrolyte at a solid interface, as investigated by using optical and scattering techniques [14,29], indicated that the adsorption time significantly influenced the amount of coated polyelectrolyte [27,30,31]. The effect of immersion time on the contact angle of multilayered film coated with PEI before dipping in Nafion solution (ethanol:water 85:15, in the absence of NaCl) was then investigated and the data are presented in Figure 3.

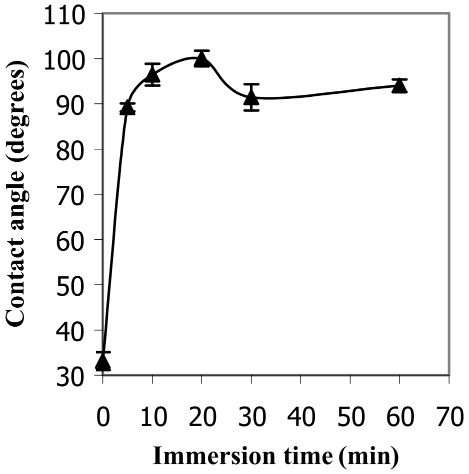

Figure 3. Contact angle of multilayered film coated with PEI before immersing in Nafion solution (using 500 mg/100mL of ethanol to water, 85:15, in the absence of salt) as function of immersion time

Results showed that the contact angle value of multilayered film having Nafion as the outermost layer abruptly increased in the initial period and attained the maximum value of 100° ± 1° within 20 min. This might be explained that the substrate surface reached the saturated adsorption [29,30]. After that period, the value slightly decreased and then approached the constant which was possibly due to the repulsion between -SO_3^- groups of Nafion causing a reduction of the amount of Nafion adsorbed onto the multilayered film. The results agreed well with those previously reported that the adsorption process of polyelectrolyte such as poly(styrene sulfonate) (PSS) and PAH was complete within 20-30 min [29-31]. The immersion time of multilayered film in the Nafion solution, was, therefore, fixed at 20 min in further experiments.

Effect of NaCl concentration added in Nafion solution

It is well known that an addition of salt into polyelectrolyte system causes deposition in thicker and loopy layers of polyelectrolyte chains due to the screening enhanced adsorption effect [9,14,30]. The response of PEI/Nafion assembly to the change of ionic strength was explored by applying Nafion solution (ethanol:water 85: 15) having different NaCl concentrations and then measuring the contact angle of the multilayered film as presented in Figure 4.

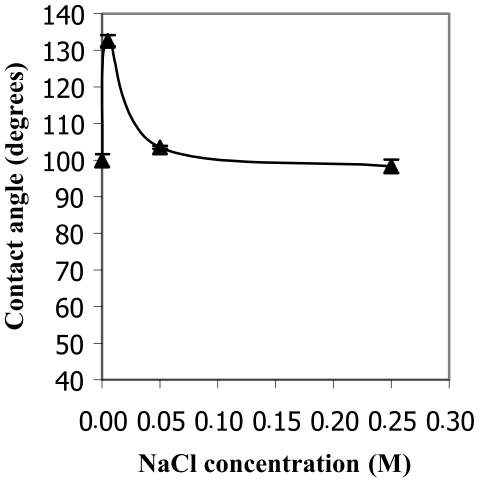

Figure 4. Effect of NaCl concentration in Nafion solution on contact angle of multilayered film having Nafion (500 mg/100 mL of ethanol to water = 85:15 and immersion time for 20 min) deposited on PEI coated particles covered on the glass substrate

In Figure 4, with increasing NaCl concentration, the contact angle of the multilayered film covered with Nafion firstly increased and then decreased when NaCl concentration changed from 5 × 10^{-3} to 5 × 10^{-1} M. This result agreed well with the previous works which reported the total thickness of PEI/Nafion bilayers as a function of NaCl concentration [9]. The small amount of added salt could screen repulsive interaction between ionic groups of $-SO_3^-$ of Nafion [9,22] which enhanced the adsorption of Nafion and caused the change in polymer chain conformation. Upon charge screening, the polymer transformed from an extended conformation to a more globular and coiled conformation that deposited far more thickly on the substrate [9]. By continue addition of salt, the reduction in thickness was generally attributed to binding competition and Coulombic shielding at the deposition surface from the highly concentrated small ions which would effectively block Nafion adsorption [9]. Though there is no noticeable precipitation or aggregation, higher salt concentrations also resulted in a gradual loss of Nafion solubility. Therefore, NaCl concentration in the Nafion solution was kept at 5 × 10^{-3} M for promoting maximum hydrophobicity of the multilayered film, i.e., 133° ± 1°. It was noticed that this contact angle value was higher than that of PTFE film (108°) [11] possibly due to the high roughness or larger surface area of multilayered film caused from latex particle deposition.

Effect of number of PEI/Nafion bilayer

Effect of the existence of PS particles in the multilayered film, having Nafion as the top layer, on the hydrophobicity of film surface was additionally confirmed. Since the previous works illustrated that the surface wettability of sequentially adsorbed polyelectrolyte layer was sensitive to the number of polycationic/polyanionic bilayers [9,31,32], the film having one to two bilayers of the PEI/Nafion combination was built-up on the substrate with or without particle deposition. The picture of a water droplet on the multilayered film surface containing PS particles and one PEI/Nafion bilayer is shown in Figure 5 (a) whereas that of the film without particle deposition is presented in Figures 5 (b). Figures 5 (c) and (d) show the similar phenomena on the films applying with two PEI/Nafion bilayers.

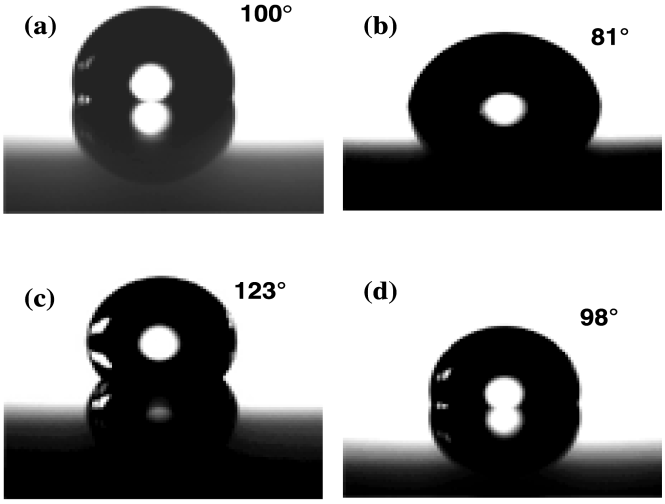

Figure 5. Contact angle of multilayered film having one PEI/Nafion bilayer as the top surface in the case of film (a) with, (b) without particle deposition and that having two PEI/Nafion bilayers in the film (c) with, (d) without particles deposition (using Nafion of 500 mg/100 mL of the mixed solvent of ethanol:water, 85:15 and immersion time for 20 min)

As expected, it was clearly observed in Figure 5 that using either one or two PEI/Nafion bilayers, the contact angle value of multilayered film containing particle deposition was higher than that of film without any particle. This could be explained in term of the increase of surface roughness or surface area on the film by PS particle layer, which would allow a high amount of Nafion adsorbed on the top layer. Results, therefore, indicated that the existence of particle influenced the amount of polyelectrolyte adsorbed on its surface and, hence, its hydrophobicity.

Effect of the number of PEI/Nafion bilayers adsorbed on the multilayered film, with or without particle deposition, on the films' contact angle was also investigated. The data obtained are plotted against the number of PEI/Nafion bilayers as shown in Figure 6.

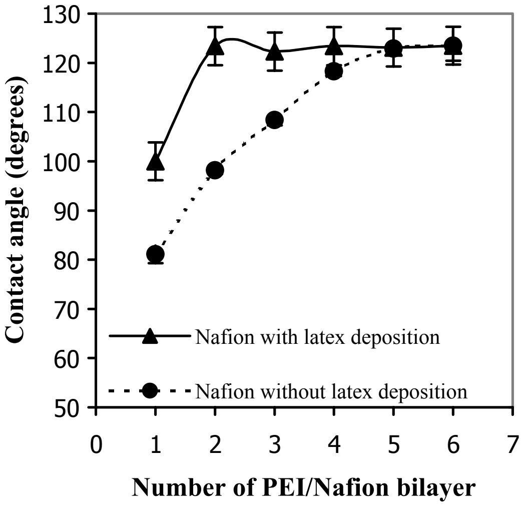

Figure 6. Effect of number of PEI/Nafion bilayers adsorbed on the film having Nafion as the outermost layer coated (▲) with and (●) without PS particles deposition (using Nafion of 500 mg/100 mL of ethanol to water, 85:15, in the absence of salt and immersion time of 20 min)

It was observed that the maximum contact angle of multilayered film with particles covered with two PEI/Nafion bilayers greatly increased to 123° ± 1° and then approached a constant value. Without particle deposition, the minimum number of PEI/Nafion bilayers required to reach this contact angle value was five bilayers. The high contact angle of the multilayered film containing five PEI/Nafion bilayers, without the latex layer, was obtained possibly due to the roughness increased from the presence of loop and tail conformations from repulsion between the amine groups in PEI and between the polar groups in Nafion molecules. From these results, it could be assumed that PS particles deposited on the substrate significantly contributed to an increase in hydrophobicity of the multilayered film. It was also of importance to emphasize that the particle deposition step could provide the thick multilayered film with less time-consuming process.

Conclusions

The adsorption of Nafion on the assembled latex film, i.e., the glass substrate coated with PEI followed by PS latex particles prepared by using the LbL technique, provided the maximum contact angle of 133^o ± 1^o. The efficiency of water repellency to the substrate surface by using Nafion depended on the effect of composition of mixed solvent, immersion time and NaCl concentration. The multilayered film roughened by latex particles deposition in the presence of 5×10^{-3} M of sodium chloride promoted the maximum contact angle of 133° ± 1°. Without using NaCl, the maximum contact angle of the multilayered film of 123° ± 1° was attained with two PEI/Nafion bilayers while the number of PEI/Nafion bilayers required to reach this value were five bilayers in the film without particle deposition.

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