Applied Surface Science 298 (2014) 142–146

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Spontaneous changes in contact angle of water and oil on novel flip–flop-type hydrophobic multilayer coatings

Go Kawamura [a,*], Tomoyuki Ema [b], Hisatoshi Sakamoto [b], Xing Wei [a], Hiroyuki Muto [a], Atsunori Matsuda [a,*]

[a] Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, Tempaku, Toyohashi, Aichi 441-8580, Japan
[b] Department of Environmental and Life Sciences, Toyohashi University of Technology, Tempaku, Toyohashi, Aichi 441-8580, Japan

ARTICLE INFO

Article history:
Received 12 December 2013
Received in revised form 21 January 2014
Accepted 23 January 2014
Available online 31 January 2014

Keywords:
Wettability
Oleophobicity
Flip–flop movement
Soil release coating
Layer-by-layer

ABSTRACT

Multilayer structures composed of poly(allylamine hydrochloride) (PAH) and Nafion were fabricated on glass substrates by layer-by-layer assembly. Some of the multilayers demonstrated spontaneous changes in contact angle of water and oil due to flip–flop movements of free sulfo groups in the Nafion layer, and the multilayers eventually possessed water repellency in air and oil repellency in water. The repellencies were enhanced by applying primer layers that were formed using SiO_2 fine particles to increase surface roughness. Compared to typical hydrophobic and oleophobic surfaces, the multilayers showed practical levels for a use as soil release coatings.

1. Introduction

Hydrophobic surfaces that show an obtuse contact angle for water have been attracting scientific and industrial attention because of their various application possibilities. The contact area of the surface with water can be extremely confined by the hydrophobicity, so various phenomena are well suppressed, for instance, friction drag, current conduction [1], bio-fouling [2], corrosion [3–5], bacterial attachment [6], and icing [7]. Numerous efforts to enhance hydrophobicity have been carried out [8–11], and the water contact angle larger than 170° has been achieved by, for example, using polyacrylonitrile nanofibers [12], or perpendicular nanopins [13]. Such kinds of hydrophobic surfaces are often associated with dirt- or water-shedding properties, and if so they are named superhydrophobic surface.

Since hydrophobic surfaces possess an oleophilic character due to the different surface tensions of water and oil, oil droplets attached to the hydrophobic surface spread and need surfactants in water to be removed. This oleophilicity of the hydrophobic surface requires frequent maintenance to keep having hydrophobicity. In contrast, hydrophilic surfaces interact significantly with water, so adsorbed oil is easily removed from hydrophilic surfaces in water. Therefore, control over wettability through contact with water has been studied and applied to soil release coatings in the textile industry [14–16]. The wettability control is achieved by the repositioning of hydrophobic and hydrophilic sites induced by the surrounding water environment. This property is named the flip–flop movement [14].

In our previous work [17], Nafion which consists of hydrophobic perfluorocarbon chains and hydrophilic sulfo groups was coated on a glass substrate as multilayered-thin films with poly(allylamine hydrochloride) (PAH). The (PAH/Nafion)-multilayer was fabricated by a layer-by-layer (LBL) method, which is simple, inexpensive, and effective technique that allows surface modification at room temperature and ambient pressure [16]. The multilayer demonstrated that a water contact angle on the surface decreased with time in humidified air because of changes in the surface wettability caused by the flip–flop movement occurring on surface of the film.

In this paper, (PAH-Nafion)-multilayer films exhibiting water repellency in air and oil repellency in water were evaluated for use as a soil release coating. In addition, a primer layer containing silica (SiO_2) nanoparticles was deposited on the glass substrate by LBL assembly in order to measure the influence of surface roughness on contact angle.

2. Experimental

PAH (M_w = ~7000, Sigma–Aldrich, Tokyo, Japan), Nafion (10 wt% in water, Wako Pure Chemical Industries Ltd., Osaka,

* Corresponding author. Tel.: +81 532 44 6791; fax: +81 532 48 5833.
E-mail addresses: gokawamura@ee.tut.ac.jp, kawamurago@hotmail.com (G. Kawamura), matsuda@ee.tut.ac.jp (A. Matsuda).

0169-4332/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2014.01.143

Japan), and poly(diallyldimethylammonium chloride) (PDDA) (M_w = 100,000–200,000, 20 wt% in water, Sigma–Aldrich, Tokyo, Japan) were used as purchased. The concentration of each polyelectrolyte in deionized water was 1.0 mg/mL. Sodium chloride (0.5 M) was added to the PAH and PDDA solutions to promote polyelectrolyte deposition. The pH of the PAH solution was adjusted to 1.6 using hydrochloric acid (HCl). Aqueous methanol solution (MeOH:H_2O = 9:1 by volume) was also used as a solvent for Nafion.

Soda-lime glass substrates (26 × 60 × 1.0 mm) were cleaned in an RCA solution (H_2O:H_2O_2:NH_4OH = 5:1:1 by volume) at 70 °C for 10 min. The glass substrates were rinsed with deionized water and dried under a flow of nitrogen (N_2) gas. The cleaned glass substrates were alternately immersed in PAH and Nafion solutions for 10 min to deposit (PAH/Nafion)$_n$ (n: the number of layers) multilayers. After each deposition step, the glass substrate was rinsed with deionized water and dried under a flow of N_2 gas. The alternate deposition of PAH and Nafion on the glass substrate was qualitatively monitored by measuring at the ζ-potential of the layers using a zeta-potential analyzer (ELS-Z1NT, Otsuka Electronics, Osaka, Japan). An average of five measurements at the stationary level was taken for each datum point. A quartz crystal microbalance (QCM, UEQ-400, USI, Fukuoka, Japan) was used to measure the weight of each layer. A gold-evaporated QCM electrode (AT-cut) with a resonance frequency of 9 MHz was used. Ultraviolet–visible (UV–vis) spectra of the multilayers were recorded with a spectrophotometer (JASCO V-560, Japan).

The contact angle of the films was evaluated by the sessile drop method using contact angle measurement equipment (DropMaster 300 with FAMAS 3.1.3, Kyowa Interface Science Co. Ltd., Saitama, Japan). Deionized water or n-hexadecane (1 μL) was used for contact angle measurements. Evaluation of the oil repellency of the surfaces was performed not only in air but also in water. The substrate with a droplet of n-hexadecane oil was placed in water, and the change in contact angle was observed.

Monodispersed SiO_2 fine particles were synthesized using the sol–gel method reported by Nishimori et al. [18]. Aqueous ammonia (0.5 M), tetraethyl orthosilicate, ethanol and sodium dodecyl sulfate (0.05 wt% against the total weight of the sol) were mixed, and then stirred at room temperature for 12 h. The cleaned substrates were alternately immersed in PDDA solution and the as-prepared SiO_2 suspension for 10 min. As before, the substrates were rinsed with deionized water and dried under a flow of N_2 gas after each immersion. The (PDDA/SiO_2)$_2$-modified substrate was then used as a substrate for (PAH/Nafion)$_n$-multilayers. The morphology and surface roughness of the (PDDA/SiO_2)$_2$-modified substrate were measured by scanning electron microscopy (FE-SEM, S-4800, Hitachi High-Technologies, Tokyo, Japan) and atomic force microscopy (AFM, Nanopics 2100, Seiko Instruments Inc., Chiba, Japan), respectively.

3. Results and discussion

The ζ-potential measurements shown in Fig. 1A support the alternative deposition of PAH and Nafion in the multilayer structures. First, polycationic PAH was partially deposited on the negatively charged glass substrate, then polyanionic Nafion was adsorbed onto the deposited PAH. After that, the charge of the layer reversed in response to each deposition of PAH and Nafion. The final deposition of Nafion made the surface charged negative, and this implied that the top surface of the substrate had hydrophilic sulfo groups upturned on hydrophobic perfluorocarbon chains (see Fig. 2 for chemical structure of Nafion). The free sulfo groups on the top surface would be able to perform flip–flop movements [17]. The deposition process of the (PAH/Nafion)$_n$-multilayers was also monitored using a QCM (Fig. 1B). The alternative deposition of PAH

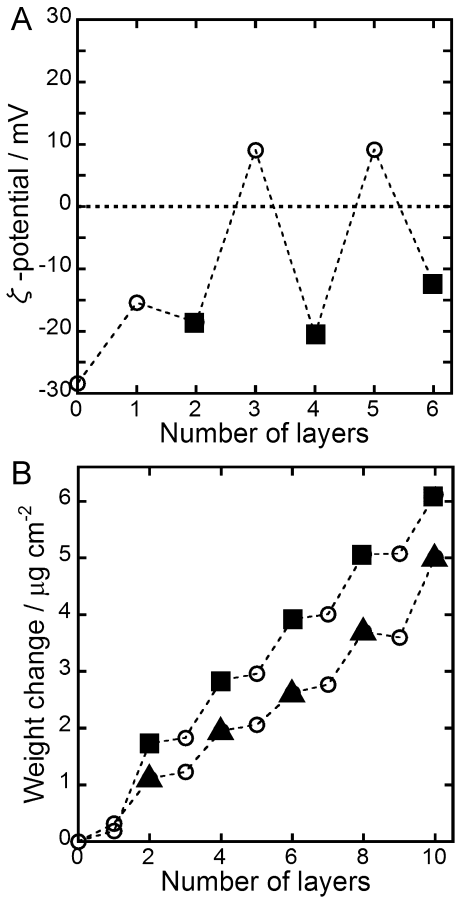

Fig. 1. (A) Changes in ζ-potential with the number of layers deposited on the substrate: PAH (○), Nafion (■) in water. (B) Changes in the amount of polyelectrolyte adsorbed calculated from the change in QCM frequency: PAH (○), Nafion (■) in water, Nafion (▲) in aqueous MeOH solution.

and Nafion was observed as stepwise increases in weight change. The amount of multilayers prepared using a Nafion water solution was larger than that of multilayer prepared from a dispersion of Nafion in an aqueous MeOH solution. The average amount of Nafion adsorbed in a single deposition was 1.12 and 0.88 μg cm^{-2} for the water and aqueous MeOH solution samples, respectively. The average amount of PAH adsorbed was about 0.1 μg cm^{-2} for both samples. Since Nafion consists of hydrophobic perfluoro chains and hydrophilic sulfo groups (Fig. 2), the conformation of Nafion in solution is highly influenced by the solvent. In water, Nafion chains aggregate through the hydrophobic interaction of fluorocarbons, so Nafion disperses in water as rod-like aggregates [19–21]. On the other hand, Nafion aggregates unravel in aqueous MeOH solution because of the decrease of surface energy between Nafion and the solvent. Accordingly, the weight change of the multilayer formed using Nafion in water was larger than that of Nafion in aqueous MeOH solution.

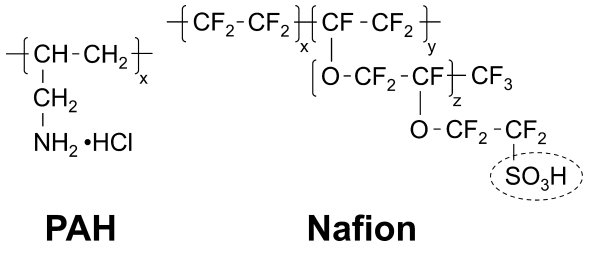

Fig. 2. Chemical structures of PAH and Nafion used for LBL assembly.