ORIGINAL ARTICLE

Polymeric ionic liquids for the fast preparation of superhydrophobic coatings by the simultaneous spraying of oppositely charged polyelectrolytes and nanoparticles

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In this work, the fabrication of superhydrophobic coatings by the simultaneous spraying of oppositely charged polyelectrolytes and nanoparticles is reported. This method is based on the polyelectrolyte layer-by-layer method but utilizes a fast simultaneous spraying approach. Superhydrophobic coatings showing water contact angles $> 150^\circ$ were obtained using poly[(1-vinyl-3-ethyl imidazolium) bis(trifluoromethane sulfonyl) imide] as a fluorinated polyelectrolyte alternative to Nafion. To obtain superhydrophobic thin films, fumed silica nanoparticles and clay nanorods were introduced into the polyelectrolyte multilayer films. The resultant superhydrophobic films showed both micro- and nano-scale features, as revealed by scanning electron microscopy and atomic force microscopy. Our polymeric ionic liquid derivatives show synthetic advantages compared with classic fluorinated polyelectrolytes.

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INTRODUCTION

Super or ultrahydrophobicity is currently the focus of a large amount of research owing to its scientific and technological importance. Nature has inspired researchers to develop superhydrophobic surfaces. Industrial applications include self-cleaning surfaces (for windows and façade paints), anti-graffiti paints, coatings that prevent snow or ice from sticking to antennas, containers that are easier to clean and biomimetic and biocompatible surfaces.¹ Different methods have been developed to obtain biomimetic superhydrophobic surfaces, which generally rely on the creation of rough micro and nanostructured surfaces covered with low surface energy molecules.^{2,3} These synthetic methods use dipping processes, vacuum deposition techniques and surface modification technologies, including diffusion, laser, or plasma processes, chemical plating, grafting or bonding hydrogel encapsulation, and bombardment with high-energy particles. Most of these methods are either expensive, substrate limited, require the use of harsh chemical treatments or cannot be easily scaled-up to large-area uniform coatings.

The polyelectrolyte layer-by-layer (LbL), or multilayer, method of thin film growth has evolved into a widely used technology.⁴ Since the mid 1990s, an exponentially increasing number of applications of this

method have been reported.⁵ The use of the LbL sequential absorption method for the assembly of ultrathin films has been reported for making ultrahydrophobic surfaces including oppositely charged polyelectrolytes and silica nanoparticles.^{6,7} However, the conventional LbL technique is quite time consuming and difficult to implement over large areas. The method of simultaneous spraying of polyelectrolyte solutions onto a substrate allows LbL thin films to be produced over large areas and in short times. However, so far, superhydrophobic layers have only been successfully made using Nafion fluorinated anionic polyelectrolytes.

Polymeric ionic liquids are a new class of polyelectrolytes that combines the chemistry of ionic liquids (cations and anions) and their physicochemical properties (ionic conductivity, thermal stability, electrochemical stability and solubility) with the improved mechanical durability and dimensional control resulting from polymerization.⁸ Polymeric ionic liquids are increasingly being used in a variety of different applications, including electrochemical devices, gas membranes, nanotechnology, materials science and analytical chemistry.^{9–13} The goal of this article is to report the fast preparation of superhydrophobic coatings by simultaneous spraying method. In this article, we also demonstrate the use of a new polymeric ionic liquid,

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poly[(1-vinyl-3-ethylimidazolium) bis(trifluoromethane sulfonyl) imide] (PEVI-TFSI) cation, as an alternative to Nafion. This functional polymer is easily synthesized in comparison with the conventional fluorinated Nafion polymers.

EXPERIMENTAL PROCEDURE

Materials

Commercially available poly(acrylic acid) (PAA, $M_w=100\,000\text{ g mol}^{-1}$, 35% solution in water), poly(sodium 4-styrene sulfonate) (PSS, $M_w=70\,000\text{ g mol}^{-1}$), poly(allylamine hydrochloride) (PAH, $M_w=70\,000\text{ g mol}^{-1}$) and perfluorinated Nafion (5% wt solution in a mixture of lower aliphatic alcohols and water) were used as received. Two different commercial nanoparticles were employed in this work: 'CAB-O-SIL TS-530' (Cabot Corporation, Boston, MA, USA), which is a high purity silica that has been treated with hexamethyldisilazane to replace many of the surface hydroxyl groups with trimethylsilyl groups, making the silica nanoparticles extremely hydrophobic, and 'Attagel 50' (Engelhard-Basf, Iselin, NJ, USA) attapulgite clay nanorods.

Synthesis of PEVI-TFSI (1). PEVI-TFSI was prepared in a two-step method as previously reported.^{13,14} First, PEVI-Br was synthesized, and then, the bromine anion was exchanged with TFSI to obtain PEVI-TFSI (1).

Preparation methods

Solution preparation. Polymer 1, Nafion, PAA, PAH and PSS solutions were prepared in water, acetone and methanol in 10 mM concentrations (per repetitive unit). The nanoparticles were added to the cationic solutions; either CAB-O-SIL TS-530 or Attagel 50 was used in concentrations ranging from 0.2 wt. % to 4 wt. %.

Substrate preparation. Glass substrates were washed before use by immersion for 1 h in Piranha solution (concentrated $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ in a 3:1 ratio). Plastic and metal surfaces were washed with distilled water.

Simultaneous spraying method. Polycation and polyanion solutions were introduced into flasks, prepared for spraying and then applied onto the surface under a constant pressure of 6 bar from a 20 cm distance. The solutions were sprayed for about 10–20 s and in some cases were then cured for 2 h at 180 °C.

Characterization methods

Contact angle measurements were carried out using a KSV CAM 200 optical tensiometer (KSV Instruments Ltd.; Helsinki, Helsinki, Finland). This apparatus is controlled by a computer that analyzes captured video images for measuring static or dynamic contact angles. The average of three measurements was taken as the value of the contact angle for each surface. A PICO SPM AFM (Agilent Technologies, Santa Clara, CA, USA) was used for molecular imaging and surface characterization. A Carl Zeiss Ultra Plus field emission scanning

electron microscope (Carl Zeiss MicroImaging, Barcelona, Spain) was used to complete the surface characterization of the modified substrates.

A Jeol JSM 5910-LV scanning electron microscope with energy-dispersive X-ray analysis (INCA-300) (Jeol Ltd., Tokyo, Japan) was used for compositional analysis of the surfaces.

RESULTS AND DISCUSSION

The aim of this work was to obtain superhydrophobic surfaces by using a modified LbL technique. This method involved changing the usual method of applying solutions: instead of the sequential step-by-step coating of a polyanion and polycation, these polymers were both applied by spraying simultaneously. This modification should make the technique fast and straightforward. With this goal, a home-built spraying system was prepared as shown in Scheme 1. It consisted of two separated flasks (one for each of the polyelectrolyte solutions) connected to two spray nozzles. To maintain a constant spraying pressure, these nozzles were connected to an air bottle. The sprayers and substrates were separated by ~20 cm. This assembly was used to both simultaneously spray oppositely charged polyelectrolytes onto prepared substrates, as well as to apply continuous films onto substrates by the LbL technique.

The solutions were sprayed for 10 s onto the substrate surfaces 20 cm away. Then, without rinsing, the substrates were cured at 180 °C for 2 h to ensure a continuous film formation. The thermal treatment should significantly improve the adhesion of the films to the sub-

Scheme 1 Home-built spraying system prepared for the simultaneous spraying of the polyelectrolyte solutions.

Scheme 2 Polyelectrolytes used in the simultaneous spraying technique experiments. A full color version of this scheme is available at *Polymer Journal* online.

Table 1 Summary of water contact angle measurements obtained by different polyelectrolyte combinations applied by simultaneous spraying onto glass substrates

Code	Polycation	Polyanion	Nanoparticles	Water contact angle (°)
a	None	None	None	35.86
b	PAH	PSS	2% Fumed SiO ₂	70
c	PEVI-TFSI	PSS	0.2% Fumed SiO ₂	124
d	PEVI-TFSI	PSS	0.4% Fumed SiO ₂	145
e	PEVI-TFSI	PSS	2% Fumed SiO ₂	165.5
f	PAH	PSS	4% clay	60
g	PEVI-TFSI	PSS	2% Nanoclay	139.5
h	PEVI-TFSI	PSS	4% Nanoclay	163
i	PEVI-TFSI	Nafion	2% Nanoclay	117.8
j	PEVI-TFSI	Nafion	4% Nanoclay	156
k	PEVI-TFSI	Nafion	2% Fumed SiO ₂	157
l	PAH	PAA	2% Fumed SiO ₂	100
m	PEVI-TFSI	PAA	2% Fumed SiO ₂	166.7
n	PAH	PAA	2% Fumed SiO ₂	100
o	PEVI-TFSI	PAA	2% Nanoclay	139.9
p	PEVI-TFSI	PAA	4% Nanoclay	163
q	PAH	Nafion	2% Fumed SiO ₂	167.9

Abbreviations: PAA, poly(acrylic acid); PAH, poly(allylamine hydrochloride); PEVI-TFSI, poly[(1-vinyl-3-ethylimidazolium) bis(trifluoromethane sulfonyl) imide]; PSS, poly(sodium 4-styrene sulfonate).

strates. It should be noted that to obtain a superhydrophobic surface, two requirements have to be fulfilled. First, the chemical composition of the surface must be hydrophobic: that is, it must have a low surface free energy. Second, the surface must have micro- and nano-scale roughness. In the previously reported LbL methods, the first requirement was met by using fluorinated polyelectrolytes such as Nafion, and the second was achieved by introducing different nanoparticles into the polyelectrolyte solutions. A similar selection of different polycations and polyanions was used in our assays. Commercially available Nafion, PSS, PAA, and PAH and the proposed polymeric ionic liquid **1** were the chosen polyelectrolytes (see Scheme 2). Polymer **1** was chosen as an alternative to Nafion because of the fluorinated nature of the TFSI counter-anion. To achieve the desired roughness, two different types of nanoparticles were tested, including fumed silica nanoparticles (CAB-O-SIL TS-530) and clay nanorods (Attagel 50). The nanoparticles were negatively charged and were added to the polycationic solution to improve their layer incorporation compatibility.

Table 1 summarizes the water contact angle results obtained from different simultaneous spraying combinations of polycations and polyanions containing the nanoparticles. Superhydrophobic surfaces are generally defined as surfaces that present a water contact angle $> 150^\circ$. Using the simultaneous spraying method, these surfaces were obtained when at least one fluorinated polycation or polyanion, such

Figure 1 Water contact angle measurements of the coatings obtained from the simultaneous spraying of polyelectrolytes. From left to right samples 'b', 'd' and 'e'. **Figure 2** Field emission scanning electron microscope images of the modified metallic substrates using sample 'e' simultaneous spraying conditions. The roughness of the surfaces can be seen with each magnification. (a) 3.22 KX; (b) 7.88 KX; (c) 15.81 KX; and (d) 26.05 KX.

as Nafion, and polymer **1** were used with a nanoparticle content $>2\%$. This can be clearly seen by comparing the results of samples b, c, d and e. In the first case (b), neither of the polyelectrolytes (PAH and PSS) was fluorinated, and although the nanoparticle content is high (2%), the water contact angles stay at low values (70°). When polymer **1** was introduced as a polycation, the water contact angle increased with the nanoparticle content to 145° and 165.5° for the 0.4% and 2% nanoparticle concentrations, respectively (Figure 1). The polymer **1** films showed a similar superhydrophobic behavior to the Nafion films. In both cases, when clay nanorods or SiO_2 nanoparticles

were used, similar superhydrophobic responses were observed as shown for cases j, k, m, p and q in Table 1.

The simultaneous spraying method was applied to different substrates. Glass slides were used as a reference in these studies, but similar results were obtained using plastic substrates (polycarbonate, polypropylene and acrylonitrile butadiene styrene (ABS) and metal substrates (stainless steel and nickel). Interestingly, the adhesion of the superhydrophobic layers to the substrates was excellent after thermal treatment in all cases except for polypropylene substrates. The adhesion of polymer **1**-containing layers was qualitatively better than those

Figure 3 Atomic force microscopy image of superhydrophobic coating 'e' onto the metal substrate. The superhydrophobic surface containing fumed silica nanoparticles.

Figure 4 Atomic force microscopy image of superhydrophobic coating cylindrical nanoclay (sample q) on a glass substrate. (a) At high magnification and (b) at low magnification.

containing Nafion. Some small differences were observed with scanning electron microscope at high resolution between the plastic and glass substrates under simultaneous spraying formulations, probably owing to the difference in adhesion to both substrates. The scanning electron microscope images show some roughness at the micro-level, as well as roughness at the nanometer scale, owing to the fumed silica nanoparticles (Figure 2). It is well known that this dual effect is responsible for the superhydrophobic behavior, as was observed in previous cases.^{2,3}

A similar micro and nanometer range roughness in the samples was observed by using AFM. As shown in Figure 3, the superhydrophobic surface obtained by using fumed silica spherical nanoparticles shows a micrometer range roughness, as well as a granular, nanometer range morphology. The AFM images of the superhydrophobic surfaces obtained using the clay nanorods show a different morphology (Figure 4), in which the cylindrical nanorods can be well distinguished on the surface. Cross sections of the glass surface at different magnifications clearly demonstrate that two levels of roughness are present: one at the micrometer scale (Figure 4a) and another at the nanometer scale (Figure 4b).

Furthermore, the chemical composition of the surface was analyzed by energy-dispersive X-ray spectroscopy. These spectra confirmed the combination of the polymeric films (indicated by the presence of 13% C, 45% O, 6% F and 1% S) and the silica nanoparticles (indicated by the presence of 20% Si and 45% O) on the treated nickel surface (15% Ni). This composition, together with the surface structure, provides the modified surfaces with the desired superhydrophobic behavior.

In conclusion, we have successfully synthesized superhydrophobic coatings by the simultaneous spraying of oppositely charged polyelectrolytes and nanoparticles. This method is based on the polyelectrolyte LbL method and is clearly faster than the step-wise approach. Our experiments showed that both the chemical nature of the surface and its topography have an important role in the final characteristics of the films. To obtain superhydrophobic surfaces, one of the polyelectrolytes must have a fluorinated moiety, and there are a minimum required number of spherical nanoparticles or clay nanorods. Polymeric ionic liquid **1** proved to be a good alternative to Nafion as a binder for the

fast preparation of superhydrophobic coatings by simultaneous spraying of oppositely charged polyelectrolytes and nanoparticles.

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