

Layer-by-Layer Deposition of Poly(diallyldimethylammonium chloride) and Sodium Silicate Multilayers on Silica-Sphere-Coated Substrate—Facile Method to Prepare a Superhydrophobic Surface

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A facile method for preparing a superhydrophobic surface was developed by layer-by-layer (LbL) deposition of poly(diallyldimethylammonium chloride) (PDDA)/sodium silicate multilayer films on a silica-sphere-coated substrate followed with a fluorination treatment. First, a silica-sphere-coated substrate that contains loosely stacked silica spheres of 600 and 220 nm was prepared and cross-linked with SiCl₄. PDDA was then alternately assembled with sodium silicate on the silica-sphere-coated surface to prepare a micro- and nanostructured hierarchical surface. Scanning electron microscopy (SEM) images verify that the deposition of a 5-bilayer PDDA/sodium silicate multilayer film leads to the formation of a micro- and nanostructured hierarchical surface. After chemical vapor deposition of a layer of fluoroalkylsilane, a superhydrophobic surface with a water contact angle of 157.1° and sliding angle of 3.1° was successfully fabricated. The easy availability of the materials and simplicity of this method might make the superhydrophobic surface potentially useful in a variety of applications.

Introduction

The superhydrophobic surface refers to these on which the water contact angles are larger than 150° and the sliding angles are less than 10°.¹ In recent decades, there have been a growing number of reports on the fabrication of the superhydrophobic surface because of its potential industrial applications in numerous aspects, such as self-cleaning surface,² marine coatings,³ anti-adhesive coatings,⁴ microfluidic channels with reduced flow resistance,⁵ and so forth. The self-cleaning superhydrophobic surface originates from the famous lotus effect of some natural leaves, which was first demonstrated by Barthlott and Neinhuis⁶ and further clarified by Jiang and co-workers.^{1b,7} The micro- and nanoscale hierarchical structures and the low-surface-energy wax epicuticula on the surface of a lotus leaf are both critically important to its self-cleaning superhydrophobic property. On the basis of this fact, the superhydrophobic surface can generally be fabricated by either increasing substrate surface area of hydrophobic materials or modification of rough surfaces to lower the surface energy.⁷

To date, a variety of methods, such as lithographic patterning,⁸ laser/plasma etching,⁹ vertical alignment of nanotubes/nanofibers,¹⁰ sol–gel method,¹¹ phase separation,¹² binary colloidal assembly,¹³ glancing angle deposition,¹⁴ and so forth,¹⁵ have been developed for the preparation of superhydrophobic surfaces. Although these methods work well for the preparation of superhydrophobic surfaces with high contact angles and low sliding angles, simple and inexpensive methods are still highly desirable for industrial applications of these kinds of surfaces.

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The layer-by-layer (LbL) assembly technique, which was developed by Decher and co-workers,¹⁶ has been proven to be a simple and inexpensive way to fabricate various kinds of surfaces with tailored chemical composition and architecture in micro- and nanoscales.¹⁷ Recently, there have been several reports concerning the use of LbL assembly technique to construct superhydrophobic surfaces.^{18–23} Shiratori and co-workers constructed superhydrophobic surfaces by first fabricating a LbL assembled hybrid film of polyelectrolyte/SiO₂ nanoparticles and then removing the organic components by calcination at 650 °C to develop an inorganic nanostructure for superhydrophobic behavior.¹⁸ Zhang and co-workers reported the use of polyelectrolyte multilayers as a preformed matrix for electrochemical deposition of gold and silver clusters to fabricate superhydrophobic surfaces.¹⁹ Rubner and co-workers mimicked the superhydrophobic behavior of the lotus-leaf structure by first treating the 100.5-bilayer poly(allylamine hydrochloride) (PAH)/poly(acrylic acid) (PAA) film in acidic solution to induce microporous structure followed by overcoating the microporous surface with silica particles.²⁰ Cho and co-workers fabricated the superhydrophobic surface by depositing silica nanoparticles on the surface of a 10-bilayer PAA-coated ZrO₂ nanoparticle/PAH film followed with a simple fluorination.²¹ Schlenoff and co-workers prepared ultrahydrophobic surfaces by a LbL assembly of fluorinated polyelectrolytes and natural nanorods.²² Taking advantage of the amplified exponential growth of PAA and polyethylenimine (PEI) in the presence of silver ions, Ji and co-workers reported a way to construct PAA/PEI-Ag⁺ films with hierarchical micro- and nanostructures for use as superhydrophobic surface after thermally cross-linking the film.²³ The above results, as well as the easy fabrication of large area films with LbL assembly technique, demonstrate that the LbL assembly technique holds great promise in fabricating superhydrophobic surfaces in a simple and inexpensive way.

LbL assembly technique enables the deposition of multilayer films on non-flat surfaces.^{17e,24} In this paper, we examined the possibility to prepare a micro- and nanostructured hierarchical surface for use as a superhydrophobic

surface by depositing LbL assembled multilayer films on substrates with microstructures. To do so, silica-sphere-coated substrate was selected to provide the microstructure and LbL deposited 5-bilayer poly(diallyldimethylammonium chloride) (PDDA)/sodium silicate multilayer film was used to provide the nanostructures on top of the microstructures. After the modification of the as-prepared micro- and nanostructured hierarchical surface with a layer of fluoroalkylsilane to lower its surface energy, a superhydrophobic surface with a water contact angle of 157.1° and sliding angle of 3.1° was obtained. The advantage of this method is that the preparative procedure is very simple and the materials used are easily available. Meanwhile, we believe that the use of sodium silicate to generate the nanostructures on top of the microstructures will provide a way to tailor the wettability of the surface by simply varying the parameters for the deposition of the PDDA/sodium silicate films.

Experimental Section

Materials. The silica microspheres with diameters of about 600 and 220 nm were synthesized using a modified Stöber method.²⁵ The silica spheres were dispersed in anhydrous alcohol. 1H,1H-,2H,2H-perfluorooctyltriethoxysilane (POTS) was purchased from Degussa. Poly(diallyldimethylammonium chloride) (PDDA) aqueous solution with a molecular weight of 100 000–200 000, silicon tetrachloride (SiCl₄), and sodium silicate were all purchased from Sigma-Aldrich. The solvents used were of analytical grade. Water purified in a Milli-Q (Milli Pore) system was used during all the experiments. All reagents were used as received.

Treatment of the Substrate. A substrate of silicon wafer (2 × 10 cm²) was immersed in a slightly boiled piranha solution (3:1 98% H₂SO₄:30% H₂O₂ mixture) for 20 min and rinsed with copious amounts of water. In this way, the wafer was hydrophilized. **Caution:** Piranha solution reacts violently with organic materials and should be handled carefully. Ag-coated quartz crystal microbalance (QCM) resonators were sonicated in ethanol and water and were dried by N₂ flow. The gold substrates were prepared by sputtering a 3 nm adhesion layer of chromium and a 100 nm layer of gold onto the cleaned glass slides. The newly prepared gold substrates were immersed in the piranha solution for several seconds, rinsed with copious amounts of water, and dried with a N₂ flow.

Preparation of the Superhydrophobic Surface. The procedure for the preparation of the superhydrophobic surface is schematically shown in Figure 1 and consists of three steps as follows.

(I) *Preparation of the silica-sphere-coated substrate.* The silica spheres used for substrate coating were dispersed in anhydrous alcohol. Before usage, the suspension was sonicated for a few minutes to disperse the silica microspheres well. The concentration of the suspension was 2.8 wt %, which contained ~90% (mass fraction) silica spheres of about 600 nm and ~10% silica spheres of about 220 nm. The deposition of the silica spheres was conducted at room temperature. The hydrophilized silicon wafer was first immersed in an alcoholic suspension of silica microspheres for a few seconds. The substrate was then withdrawn from the suspension at a speed of 1.5 mm/s. Under these conditions, the alcoholic solvent volatilized rapidly, leading to the deposition of the silica spheres onto the substrate. A silica-sphere-coated substrate was obtained by repeating the deposition process three times. To further improve the adhesion of the spheres to the substrate, we transferred the silica-

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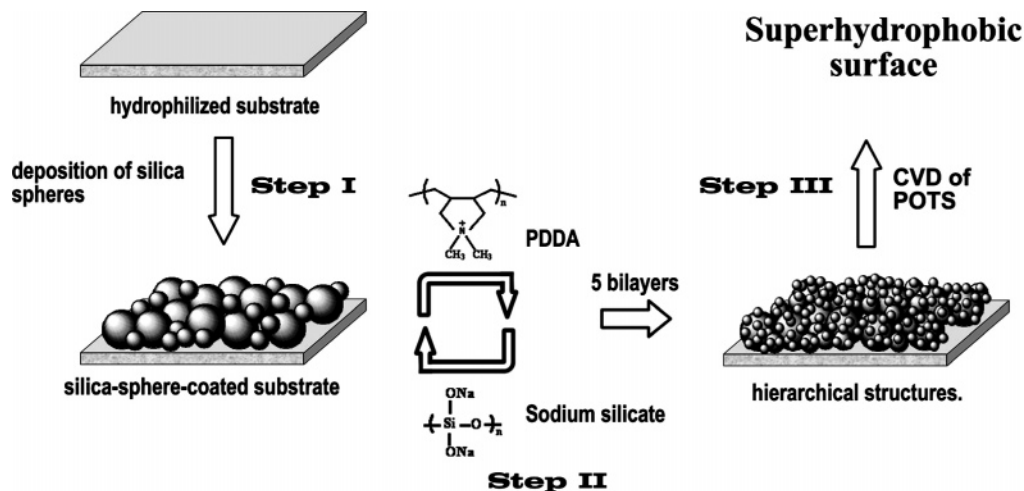


Figure 1. Schematic illustration of the fabrication of a superhydrophobic surface.

sphere-coated substrate to a toluene solution of SiCl_4 (1 wt %) for half an hour, followed by washing with toluene, hydrolyzing in water, and drying with a N_2 flow. In this way, a cross-linked stable silica-sphere-coated substrate was obtained.

(II) *LbL Deposition of PDDA and Sodium Silicate.* The silica-sphere-coated substrate was first immersed in a PDDA aqueous solution (1.0 mg/mL) for 20 min to render the substrate positively charged, followed by rinsing with water twice for 1 min each time and drying with N_2 flow. The substrate was then transferred to an aqueous sodium silicate solution (154 mM, pH 11.6) for 10 min, rinsed with water twice for 1 min each time, and blown dry with N_2 flow. By repeating the above deposition processes in a cyclic fashion, we can fabricate a multilayer film of PDDA/sodium silicate. To fabricate a superhydrophobic surface, we deposited a 5-bilayer PDDA/sodium silicate multilayer film with sodium silicate as the outmost layer. Here, each bilayer refers to the deposition of one PDDA layer and one sodium silicate layer on the substrate.

(III) *Chemical Modification of the Substrate.* The modification was carried out by chemical vapor deposition (CVD) of the POTS. The silica-sphere-coated substrate deposited with PDDA/sodium silicate multilayer film was placed in a sealed vessel, on the bottom of which was dispensed a few drops of POTS. There was no direct contact between the substrate and the drops. The vessel was put in an oven at 120 °C for 2.5 h to enable the vapor of POTS to react with the OH groups on the substrate surface. Finally, the substrate was taken out of the vessel and placed in an oven of 150 °C for another 1.5 h to volatilize the unreacted POTS molecules on the substrate.

Characterization. QCM measurements were taken with a KSV QCM-Z500 using quartz resonators with both sides coated with Ag ($F_0 = 9$ MHz). The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB250 (VG Microtech., UK). Scanning electron microscopy (SEM) images were obtained on a JEOL JSM 6700F field emission scanning electron microscope. Atom force microscopy (AFM) images were taken on a Nanoscope IIIa atom force microscope (Digital Instruments, Santa Barbara, CA). The static contact angles and sliding angles of the as-prepared surfaces were measured with a commercial contact angle system (DataPhysics, OCA 20) at ambient temperature using a 4 μL water droplet as the indicator.

Results and Discussion

Preparation of PDDA/Sodium Silicate Multilayer Films by the LbL Assembly Technique. Sodium silicate is a common, inexpensive, and negatively charged chemical

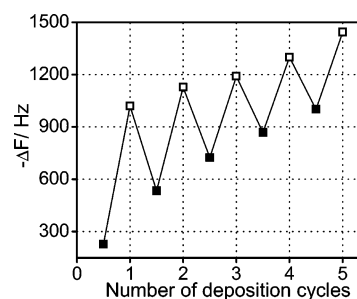


Figure 2. QCM frequency decrease ($-\Delta F$) of the alternative deposition of PDDA (■) and sodium silicate (□).

consisting of linear, branched, and ring-shaped oligomers that can be denoted in the form of a linearly condensed structure, as shown in the scheme of Figure 1.²⁶ PDDA has been used frequently as a linear polycation for electrostatic LbL preparation of multilayer films. To verify that PDDA and sodium silicate could be alternately assembled by LbL assembly technique to prepare PDDA/sodium silicate multilayer films, we first fabricated the multilayers on the Ag-coated QCM resonators. QCM was employed to monitor the deposition process. As shown in Figure 2, the decreases in QCM frequency are plotted as a function of the layer number for PDDA and sodium silicate. The deposition of the PDDA/sodium silicate multilayers was dominated by an adsorption–desorption process. After each deposition step of sodium silicate layer, the average frequency decrease was 530.6 ± 124.2 Hz, which indicated that sodium silicate deposited successfully on the substrate. However, when PDDA was adsorbed, the frequency increased with an average value of 377.4 ± 85.5 Hz, which indicated a desorption of the previously deposited species. A likely explanation for the adsorption–desorption process is the partial removal of sodium silicate from the surface to the PDDA solution during the PDDA deposition steps. Despite the desorption process, one bilayer of sodium silicate/PDDA leads to an average net frequency decrease of 148.1 ± 29.6 Hz, confirming the deposition of sodium silicate/PDDA multilayer films. The

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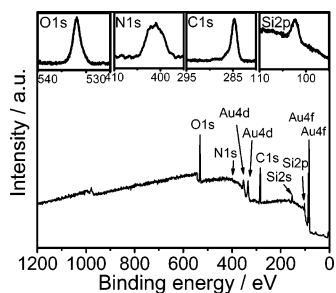


Figure 3. XPS spectra of a 5-bilayer as-fabricated PDDA/sodium silicate multilayer on a gold substrate.

LbL deposition of PDDA and sodium silicate was based mainly on electrostatic interaction as a driving force.

Simultaneously, the deposition of PDDA/sodium silicate multilayer films was also confirmed by the XPS measurements. The XPS spectra of a 5-bilayer PDDA/sodium silicate multilayer are shown in Figure 3. To avoid the influence of the silicon from the substrate, we deposited the PDDA/sodium silicate multilayer film for XPS measurements on a gold substrate instead of a silicon wafer. The peaks at 82.9, 86.9, 333.9, and 353.0 eV correspond to the binding energies of Au 4f_{7/2}, Au 4f_{5/2}, Au 4d_{5/2}, and Au 4d_{3/2}, respectively.²⁷ The peaks at 102.0 and 153.1 eV are characteristic Si (IV) 2p and Si (IV) 2s signals, respectively.²⁸ The peak of O 1s locates at 531.9 eV. The Si:O atomic ratio of was 1:3.7 as calculated from the relative peak areas after correction of sensitivity factors. This value is close to that in sodium silicate of (Na₂SiO₃)_n when considering the experimental errors caused by the XPS itself. This result confirmed the incorporation of sodium silicate into the multilayer films. The signals of N 1s and C 1s appear at 403.3 and 284.7 eV in the XPS spectra, respectively, confirming the incorporation of PDDA in the multilayer films. The XPS data, together with the QCM measurements, endorsed the successful deposition of the PDDA/sodium silicate multilayer films by the LbL assembly technique.

Deposition of PDDA/Sodium Silicate Multilayers on Silica-Sphere-Coated Substrate. The deposition of PDDA/sodium silicate multilayer films was performed on the silica-sphere-coated substrate to prepare superhydrophobic surfaces. SEM images shown in Figure 4 give straightforward evidence for the successful deposition of PDDA/sodium silicate multilayer films on the microstructured surface and reveal the formation of the hierarchical micro- and nanostructures. Figure 4a is the SEM image of the as-prepared silica-sphere-coated substrate surface, which was obtained after the deposition of the silica spheres three times. The silica spheres were randomly distributed on the substrate, with the large spheres of about 600 nm being segregated by the little ones of 220 nm. The surface of the individual silica spheres is smooth. The as-prepared silica-sphere-coated surface was quite irregular and full of interstices. In addition to the irregularity of the spheres, the rapid evaporation of the alcoholic solvent during the deposition process shortened the time for the silica spheres to organize regularly onto the substrate. Therefore, the irregularity in sphere sizes and the

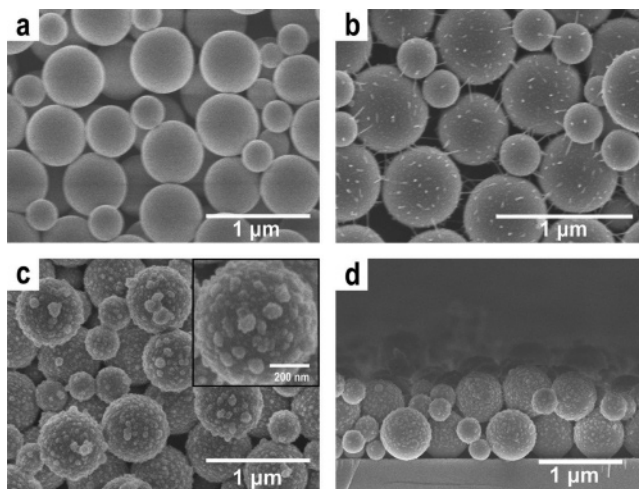


Figure 4. SEM images of the silica-sphere-coated surface: (a) as-fabricated; (b) after cross-linking with SiCl₄; (c) after LbL deposition of 5-bilayer PDDA/sodium silicate multilayers on (b); (d) cross-sectional view of the silica spheres in (c). Inset: magnified view of a single silica sphere.

rapid evaporation of the solvent favored the irregular arrangement of the spheres and increased the surface roughness. The SEM image of the silica-sphere-coated surface after the cross-linking with SiCl₄ is shown in Figure 4b. After cross-linking, the surface roughness of the spheres increases with the observation of tiny particles on sphere surfaces and nanowires connecting adjacent silica spheres. The cross-linking improved the stability of the silica spheres on the substrate compared with the non-cross-linked ones as a lengthy immersion in water cannot remove the spheres from the substrate. Such a rough surface can subsequently serve as a basic substrate for the LbL deposition of PDDA/sodium silicate multilayer films to fabricate hierarchical structures. As shown in Figure 4c, many nanopillae can be observed on the surface of the silica spheres after the deposition of a 5-bilayer PDDA/sodium silicate multilayer film. These nanopillae are discretely distributed PDDA/sodium silicate multilayers, having a size of about 40–70 nm. The formation of nanopillae rather than smooth film after the deposition of 5-bilayer PDDA/sodium silicate film can be attributed to the island-like growth of sodium silicate during the initial nucleation stage of its deposition because sodium silicate is more strongly bonded to itself than to the substrate. The formation of nanopillae on a smooth silicon substrate was also found after the deposition of 5-bilayer PDDA/sodium silicate film on it. AFM measurements showed that the as-prepared silica-sphere-coated substrate had a root-mean-square (RMS) roughness of 127 nm. After cross-linking with SiCl₄ and deposition with a 5-bilayer PDDA/sodium silicate multilayer film, the RMS roughness increased dramatically to 246 nm. The nanopillae combined with the underneath submicrometer spheres constituted the hierarchical micro- and nanostructures and further enhanced the roughness of the surface. The cross-sectional view of the as-prepared hierarchical structures in Figure 4d reveals that the film consists of two layers of large spheres after deposition in a silica sphere suspension three times. The thickness of the film is about 1.2 μm. Meanwhile, it can be seen clearly that all silica spheres deposited on the substrate are covered completely by the nanopillae,

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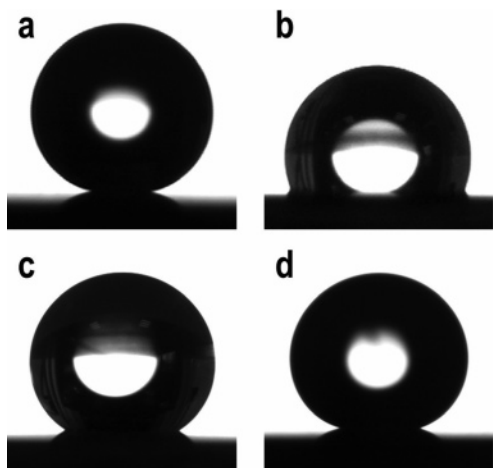


Figure 5. Shapes of water droplets (4 μL) on the POTS-modified substrates: (a) silica-sphere-coated silicon surface after deposition of 5-bilayer PDDA/sodium silicate multilayers (CA = 157.1°); (b) smooth silicon wafer (CA = 110°); (c) silica-sphere-coated surface without the deposition of PDDA/sodium silicate multilayers (CA = 140°); (d) 600 nm monodispersed silica-sphere-coated silicon surface after the deposition of 5-bilayer PDDA/sodium silicate multilayers (CA = 147°).

indicating that during the LbL deposition, PDDA and sodium silicate can penetrate through the interstices and deposit onto the surface of silica spheres.

Wettability of the Superhydrophobic Surface. Up to now, a hierarchically structured surface comprising submicrometer silica spheres and nanometer papillae of PDDA/sodium silicate films has been successfully fabricated. Chemical vapor deposition of fluoroalkylsilane POTS on the hierarchically structured surface was finally performed to prepare a superhydrophobic surface. The wettability of the surface was characterized by the contact angle instrument using a 4 μL water droplet as the indicator. As shown in Figure 5a, the water contact angle reached as high as 157.1°, indicating a superhydrophobic surface was obtained. Furthermore, the sliding angle on such a surface was as low as 3.1°, which means the water droplets on the surface could roll off easily. Therefore, the as-fabricated hierarchically structured surface has a lotus-like property, which can be used as the self-cleaning surface. As a comparison to the hierarchically structured surface, the water contact angles on the smooth silicon wafer and silica-sphere-coated surface (without PDDA/sodium silicate deposition) after CVD of POTS were 110 and 140° (images b and c of Figure 5), respectively. Accordingly, under the condition that the chemical composition of the surfaces is identical, one can confirm that the hierarchical structures based on the silica spheres and the nanopapillae of PDDA/sodium silicate multilayers contribute to the large contact angle. The Cassie–Baxter equation can explain the superhydrophobicity of the hierarchical surface with the deposition of PDDA/sodium silicate multilayers: $\cos \theta_r = f_1 \cos \theta_s - f_2$.²⁹ The equation assumes that the water droplet does not completely wet the rough substrate. Air is trapped in the interstices of the rough surface, and the droplet interacts with the composite surface that consists of solid material and air pockets. Here, θ_r (157.1°) is the apparent contact angle on the rough surface

modified with POTS; θ_s (110°) is the contact angle on the POTS modified smooth silicon surface; f_1 and f_2 are the fractions of solid surface and air in contact with water, respectively, that is, $f_1 + f_2 = 1$. It is recognized from the equation that increasing the fraction of air (f_2) increases the water contact angle on the rough surface (θ_r). According to the equation, the f_2 value of the hierarchical surface is calculated to be 0.88, which indicates that 88% of the surface is occupied by the air. Therefore, the water contact angle on the hierarchical surface increased significantly.

At the same time, the irregularity of the sphere sizes also contributed to the large roughness of the hierarchical surface and enhanced its water contact angle. When 600 nm monodispersed silica spheres instead of the dual sized spheres of 600 and 220 nm was used to fabricate silica-sphere-coated substrate, the water contact angle was 147° (Figure 5d) and the sliding angle was larger than 30° after the LbL deposition of 5-bilayer PDDA/sodium silicate films and the following CVD of POTS. The small water contact angle and the large sliding angle in this case are possibly attributed to the more ordered nature of the hierarchical surface when monodispersed silica spheres were used to fabricate the microstructures.³⁰

The wettability of the hierarchically structured surface is dependent on the number of PDDA/sodium silicate bilayers. When 10-bilayer PDDA/sodium silicate multilayer films were deposited on the silica-sphere-coated surface followed with CVD of POTS, the water contact angle and sliding angle are about 156.8 and 4°, respectively. With a further increase in the number of bilayers to 15, although the contact angle does not change obviously, the sliding angle reaches as high as 10°. With more bilayers of PDDA/sodium silicate films deposited on the silica-sphere-coated surface, the coverage of the nanopapillae increases and a more compact layer of nanopapillae forms (see Supporting Information). The compact nanopapillae on the silica-sphere-coated surface decrease the surface roughness and, accordingly, do not favor the construction of a superhydrophobic surface with a decreased sliding angle. Therefore, a 5-bilayer PDDA/sodium silicate film is well-suited to fabricate a superhydrophobic surface with a large water contact angle and low sliding angle.

Conclusions

In the present study, we show that PDDA/sodium silicate multilayer films can be deposited by a LbL assembly technique on silica-sphere-coated surface to form a micro- and nanostructured hierarchical surface. After chemical vapor deposition of a layer of fluoroalkylsilane, a superhydrophobic surface is successfully fabricated. The present method for preparing a superhydrophobic surface has the advantage of simplicity in fabrication, easy availability of the materials, and applicability to prepare large area surface. This kind of superhydrophobic surface can find potential applications as self-cleaning surfaces, anti-adhesive coatings, and so forth.

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Supporting Information Available: SEM images of the silica-sphere-coated surface after LbL deposition of 10 and 15 bilayer PDDA/sodium silicate multilayer films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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