Preparation of Superhydrophobic Surfaces by Cauliflower-Like Polyaniline

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ABSTRACT: Cauliflower-like polyaniline (PANI) was successfully prepared using an interfacial polymerization method. By modification with polydimethylsiloxane (PDMS) using chemical vapor deposition method, the surface wettability of cauliflower-like PANI can be tailored to be superhydrophobic with a water contact angle of 160.4°. The deposition of the low-surface-energy silicon coating originated from PDMS pyrolysis on the cauliflower-like PANI was confirmed by X-ray photoelectron spectroscopy and Fourier Transform Infrared Spectroscopy. The changes in thermal stability and conductivity of the as-prepared PANI before and after PDMS treatment were also investigated by thermogravimetric analysis and using a four-probe method. Compared with nanofiber-shaped PANI by electrodepositing polymerization, the PDMS-treated cauliflower-like PANI has superior surface wettability. Our study may open a new way for fabrication of superhydrophobic surfaces by developing novel nanostructured PANI. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

Superhydrophobic surfaces, characterized by a water contact angle (CA) higher than 150°, have attracted considerable attention in both academy and industry because of their potential applications such as in the prevention of adhesion of snow to antennas and windows, self-cleaning traffic indicators, metal refining, stain-resistant textiles.[1,2] To fabricate superhydrophobic surfaces, a typical procedure is to create a rough surface covered with low surface energy molecules, such as fluoroalkylsilanes,[3] or to roughen the surface of hydrophobic materials. So far, a number of artificial superhydrophobic surfaces have been developed especially by controlling the geometrical structures of solid surfaces via various approaches such as lithographic methods,[4–6] template-based extrusion methods,[7–10] layer-by-layer assembly,[11,12] electrospinning,[13,14] etc. In addition to these methods, electrodepositing methods are inexpensive, fast, and easy to use.[15] In our recent study, we also have reported the fabrication of superhydrophobic conjugated microporous polymers and activated carbon-coated sponges using a dip-coating method.[16–19] To date, several kinds of conductive polymers such as polythiophene,[20] polyaniline (PANI),[21–24] polyalkylpyrrole,[25] and its derivatives[26] have been employed for fabrication of superhydrophobic surfaces by electrochemical methods. Among these conductive polymers, PANI has been extensively studied owing to

their potential applications for a wide range of fields such as light-emitting diodes, electromagnetic shielding devices, anticorrosion coatings, and chemical/electrochemical sensors, conducting molecular wires.[27] In recent years, one-dimensional PANI nanostructures, such as nanofibers, nanobelts, rods, and tubes,[28–30] have been developed by various synthesis strategies.[31] These PANI nanostructures make it possible to generate macroscopically rough surface, which facilitates to fabricate the superhydrophobic surfaces. However, only a few examples of superhydrophobic surfaces-based PANI has been reported so far.[32,33] Different from these PANI-based superhydrophobic surfaces constructed by nanofiber-shaped PANI as well as lowing its surface energy by incorporation of fluoro-moieties into PANI chains, in this work, we report for the first time for fabrication of superhydrophobic surfaces by developing a new kind of cauliflower-like PANI through interfacial polymerization. By surface modification with polydimethylsiloxane (PDMS) using chemical vapor deposition method (CVD), the cauliflower-like PANI shows excellent surface superhydrophobicity with a water CA of 160.4°. For comparison purpose, we also prepared superhydrophobic surfaces by creation of nanofiber-shaped PANI by electrodepositing polymerization, which only shows a water CA of 151.6°. Our study may open a new way for the fabrication of superhydrophobic surfaces by developing novel nanostructured PANI.
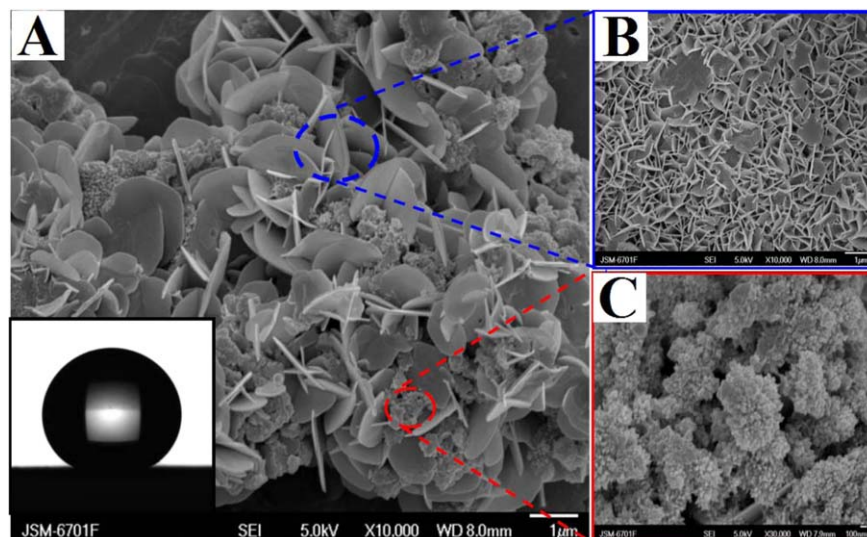
Figure 1. (A) Low-magnification SEM image of the as-prepared PANI. Inset is the water CA measurement of PDMS-treated PANI. (B,C) High-magnification SEM images of the selected area marked in (A). Scale bar: (A,B): 1μm. (C): 100 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

The aniline monomer (Alfa) was purified by reduced pressure distillation. Ammonium peroxydisulfate (APS) was purchased from Sigma-Aldrich.

Experimental Procedure

Aniline of 0.01 mol was dissolved in 50 mL toluene (solution A) and APS (0.57 g) was dissolved in hydrochloric acid solution (1M, solution B). Then solution B was carefully added into solution A with vigorous stirring. After 5 h, the aqueous phase product was collected and continuously washed with acetone and water several times followed by drying at 60°C overnight.

PANI was synthesized on the indium tin oxides glass (ITO) using electrodepositing method.[34] The experiment was carried out in a single two-electrode cell using Platinum sheet as the counter-electrode and commercial ITO as the working electrode. Before electrodepositing, ITO was washed with HCl/NH$_3$ solution (1M), distilled water, and ethanol, respectively. Electrodepositing solution containing 0.25M aniline and H$_2$SO$_4$, 0.1 mg FeCl$_3$ was deoxidized for 30 min. Subsequently, PANI was formed on the surface of ITO under 5 V voltage. The PANI film on ITO was washed by acetone, distilled water and dried at 40°C.

To fabricate superhydrophobic PANI, the PANI powder or PANI film on ITO with a piece of PDMS (Silygard 184, Dow Corning) film was sealed in weighing bottle and then dried at 80°C for 72 h.

Characterization

The morphologies of samples were examined by scanning electron microscopy (SEM) using a field emission gun scanning electron microscope (JSM-6701F, JEOL) after coating with Au film. Water CA measurements for samples were performed on a contact angle meter (DSA100, Kruss Company, German). X-ray

photoelectron spectroscopy (XPS) analysis was performed on a PHI-5300ESCA spectrometer (Perkin-Elmer). Solid state infrared spectra were recorded from in the range of 2000–600 cm^{-1} using the KBr pellet technique on a FT-Raman Module (Nicolet, America) instrument. Thermogravimetric analysis (TGA) was performed under a nitrogen flow rate of 20 mL min^{-1} using a Perkin-Elmer TG/DTA-6300 instrument evolved during sample heating. The sample was heated from room temperature to 800°C at 10°C min^{-1}. The electrical conductivity of PANI was determined by the conventional four-point method on KDY-1. The crystalline property was measured by X-ray powder diffraction (XRD) on a Rigaku with a Cu tube source and scans were taken from 2θ at 10° to 60°.

RESULTS AND DISCUSSION

The morphology of the as-prepared PANI was investigated by SEM. As shown in Figure 1(A), blooming cauliflower-like morphology was observed. From the high-magnification SEM image, the surface morphology of PANI was composed of loosely packed flakes just like "petal" [Figure 1(B)] by combination with aggregated granules like "flower bud" [Figure 1(C)]. Usually, using the aqueous solution as a media, agglomerated PAIN granules were obtained. While in interfacial polymerization performed in an aqueous/organic biphasic system, the initial formation of PAIN is not subjected to further polymerization, thus the secondary growth stage is suppressed and only PANI nanofibers are formed.[35] Interestingly, however, in our study, leaf-like PANI was also obtained in this polymerization process. Fan et al.[36] demonstrated that polymerization of aniline to form leaf-like PANI happened on the periphery of the existing PANI nuclei. Different from the conventional interfacial polymerization, we added doping agents into the organic phase during which the polymerization of aniline formed PANI in incompatible phases, resulting in the unique cauliflower-like morphology.
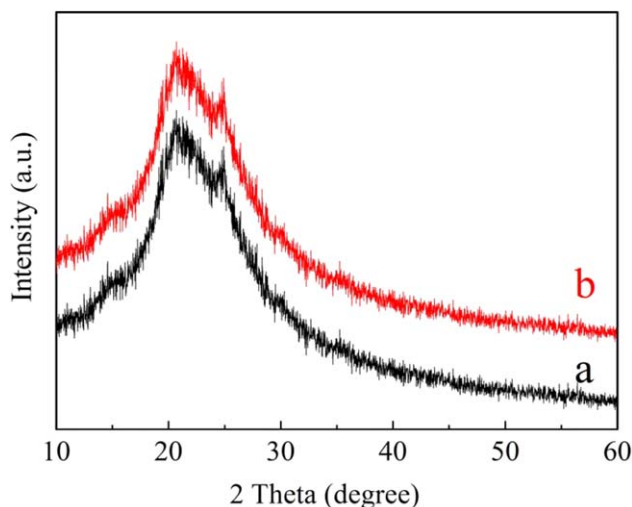
Figure 2. XRD patterns of the as-prepared PANI (a) before and (b) after PDMS treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Recently, superhydrophobic PANI with nanostructures has attracted considerable attention because of the potential applications in drug delivery, micro-fluidic devices, chemical and biological sensors, etc.[37–40] Extensive studies have revealed that the superhydrophobicity of a solid surface is controlled by the surface free energy and roughness and it is usually enhanced by surface roughness. In generally, superhydrophobic surfaces can be obtained by creating micro/nanostructures on a hydrophobic surface or modifying a rough surface by materials with low surface free energy.[6] From the result of SEM images, such obvious micro/nanostructure of as-prepared PANI would facilitate the creation of superhydrophobic surfaces. However, because of its hydrophilic nature, the as-prepared PANI shows poor surface wettability. Thus, to enhance its surface wettability, coating with low-surface-free-energy materials was reported to result in a significant improvement on the hydrophobicity of materials. In this case, PDMS (a typical low-surface-free-energy material) was used to improve the surface wettability of as-prepared PANI. As expected, The PDMS-treated PAIN exhibits excellent surface superhydrophobic property with a water CA of 160.4° [Figure 1(C) inset] and we will discuss later.

To investigate the effect of PDMS on the structure of as-prepared PANI, XRD was performed. As shown in Figure 2, an obvious broad peak at 20° and another one at 25° were observed, indicating the amorphous nature of PANI.[41] For PDMS-treated PANI, it shows the similar peak pattern and position, which suggests the structure of PANI was not changed after PDMS treatment. The surface chemical composition of as-prepared PANI before and after PDMS treatment was also studied by XPS measurement. As shown in Figure 3(A), the peaks at 296, 411, and 543 eV are attributed to C1s, N1s, and O1s, respectively, which is well in accordance with the analysis in literatures.[42] For PDMS-treated PANI, all peaks of the as-prepared PANI were observed and a new peak appeared at 102.69 eV, which is attributed to Si2p,[43] corresponding to 7.66 at.% silicon.

The IR spectra of as-prepared PANI before and after PDMS treatment were shown in Figure 3(B). For as-prepared PANI, the characteristic peaks at 1580 and 1490 cm^{-1} should be assigned to C=C stretching mode of the quinoid rings and benzenoid rings, the peak at 1290 cm^{-1} is attributed to C-N stretching vibration of the benzenoid ring and the peak at 1130 cm^{-1} corresponds to C-H aromatic in-plane bending, as seen elsewhere.[33] For the IR spectra of PDMS-treated PANI, the infrared analysis result shows that the characteristic groups of PANI exist in the product. However, a double peak at near 800 cm^{-1} appeared for PDMS-treated PANI, which is attributed to Si-O-Si symmetrical stretching vibration.[32] Both the XPS and FT-IR results suggest that the silicon moieties originating from PDMS has been introduced onto the surface of as-prepared PANI. During the CVD process, the thermal pyrolysis of PDMS would lead to the cleaving of Si-O bond to some extent and generate short PDMS chains to form a conformal layer on the surface of as-prepared PANI and subsequently to crosslink, resulting in a silicon coating on the surface of PANI
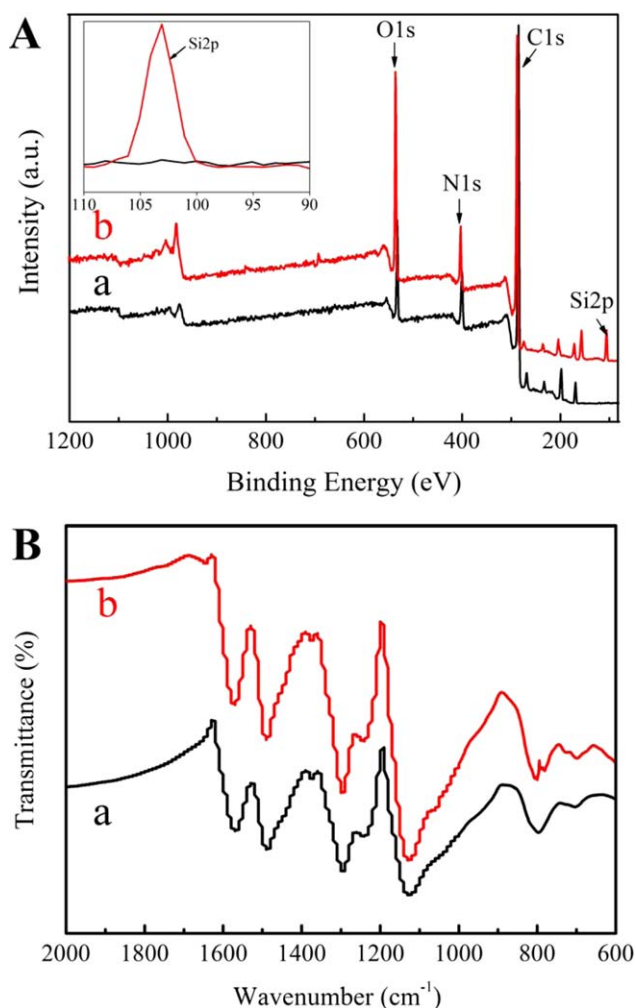

Figure 3. (A) XPS patterns of as-prepared PANI (a) before and (b) after PDMS treatment. (B) FT-IR spectra of the as-prepared PANI (a) before and (b) after PDMS treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
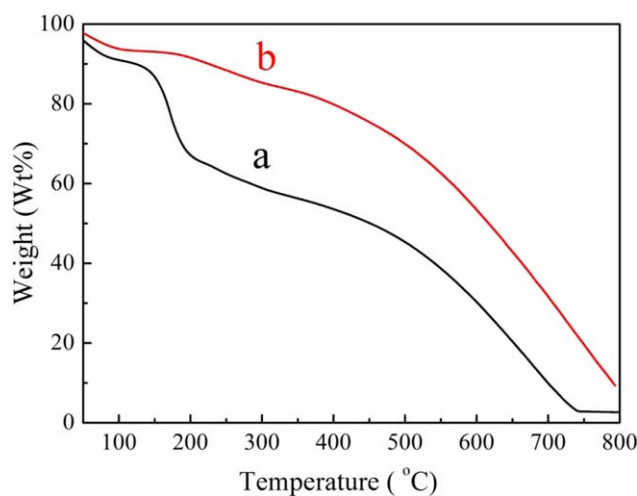
Figure 4. TGA curves of the as-prepared PANI (a) before and (b) after PDMS treatment. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
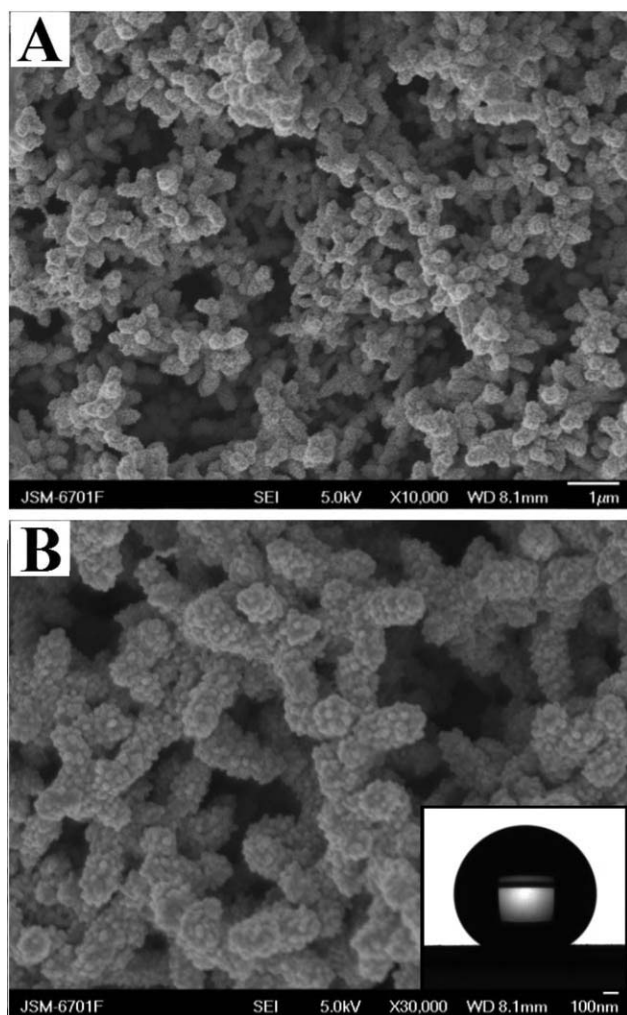

Figure 5. (A) Low-magnification and (B) high-magnification SEM image of PANI fabricated by electrodepositing method. Inset is the water CA measurement of PDMS-treated PANI fabricated by electrodepositing method. Scale bar: (A): 1 μm. (B): 100 nm.

microstructures.[44] Thus, the surface superhydrophobicity of PDMS-treated PANI should be attributed to the low surface free energy of silicon-coating on the surface and the surface roughness of as-prepared PANI as seen in SEM images.

The thermal stability of as-prepared PANI before and after PDMS treatment was investigated by TGA. As shown in Figure 4, both PANI and PDMS-treated PANI showed a very small weight loss below 100°C, implying a loss of moisture. The first obvious weight loss for PANI started at 150–200°C with the weight loss of 19.59 wt %, which is attributed to escape of doping agents.[45] After 400°C, the weight loss should be attributed to the decomposition of polymer linker of PANI. For PDMS-treated PANI, in view of the fact that the weight loss was obviously lower than that of PANI, that is, the treatment of PANI with PDMS resulted in an increasing in thermal stability. This phenomenon should be attributed to the high thermal stability of silicon-coating originating from PDMS on the surface of PANI, which is in accordance with the analysis of XPS and FT-IR, resulting in the increasing of thermal stability. The effect of PDMS on the conductivity of PANI was also investigated using a four probe method. The conductivity was decreased from 8.62 S m^{-1} for PANI to 5.83 S m^{-1} for PDMS-treated PANI, which should be attributed to the poor conductivity of silicon-coating on the surface of PANI.

For comparison purpose, we fabricated PANI on ITO substrate by electrodepositing method. After modification with PDMS in the same CVD method, the surface wettability was also changed to be superhydrophobic with a water CA of 151.6°. It can be seen from the SEM image (Figure 5) that the PANI synthesized by electrodepositing method is composed of agglomerated polymer particles with a size ranging from 50 to 90 nm in diameter. As expected, such rough microstructure of PANI synthesized by electrodepositing method facilitates the creation of superhydrophobic surfaces. However, compared with PANI synthesized by electrodepositing method, it is clearly seen that the PANI fabricated by interfacial polymerization method possesses distinct micro/nano structure that is composed of loosely packed flakes and aggregated granules. Thus, modification with the same low-surface-free-energy material, PANI fabricated by interfacial polymerization method has a relatively higher water CA and superior surface wettability than that of PANI synthesized by electrodepositing method because of this unique textured structure.

CONCLUSIONS

In summary, PANI with hierarchical micro/nanostructures was successfully prepared by an interfacial polymerization of aniline in the presence of hydrochloric acid and APS. The resulting PANI shows distinct cauliflower-like morphology. With surface modification by PDMS, the wettability of as-prepared PANI can be tailored to be superhydrophobic to water. Because of the silicon-coating originated from PDMS on the surface, the thermal stability of as-prepared PANI was increased, whereas the conductivity was decreased after PDMS treatment. Compared with nanofiber-shaped PANI by electrodepositing polymerization, the PDMS-treated cauliflower-like

PANI has superior surface wettability because of its unique morphology. Our study may provide a possibility of fabrication of novel hierarchical micro/nanostructures of PANI with superhydrophobic property.

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