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# Conductive Super-Hydrophobic Surfaces of Polyaniline Modified Porous Anodic Alumina Membranes

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A conductive polymer polyaniline (PANI) was employed to achieve surfaces of both super-hydrophobic and conductive on NaOH etched porous anodic alumina (PAA) membranes. The surfaces exhibit micro- and nanostructures. In the PANI modified PAA membrane, PANI is mainly emeraldine. After the membrane was immersed in HCl, the content of the protonated nitrogen increased, which increased the conductivity.

**Keywords:** Super-Hydrophobic, Micro- and Nanostructure, Polyaniline, Porous Anodic Alumina, Surface Chemistry.

## 1. INTRODUCTION

Super-hydrophobic surfaces, whose static water contact angles (CAs) are greater than 150°, have attracted much of current interests due to their unique structures and properties.[1] Generally, such surfaces can be effectively achieved by combining appropriate surface roughness[2–6] with compounds of low surface free energy.[3a, 3b, 7, 8] Among the previous publications, compounds containing fluorine, such as fluoroalkysilane[3a, 3b, 7] and polytetrafluoroethylene,[8] were often used as the surface modification agents. However, they are of high cost and/or not environmental friendly, which limit their applications. Non-fluorine compounds are desired. If functional compounds can be attached, functional surfaces may be obtained. Herein, we report conductive super-hydrophobic surfaces of polyaniline (PANI), a conductive polymer with general surface free energy, modified porous anodic alumina (PAA) membranes. Sodium hydroxide (NaOH) etched PAA membranes possessed micro- and nano-structures, and the surfaces of the PANI modified PAA membranes are super-hydrophobic. It is more important that the surfaces of both super-hydrophobic and conductive were successfully achieved, after the PANI modified PAA membranes were immersed in chloride acid (HCl).

## 2. EXPERIMENTAL DETAILS

Commercial PAA membranes, with an average pore diameter of 235 nm (Whatman Co., England), were etched in 3 mol · L$^{-1}$ NaOH solution for a certain period of time. 1.00 g of emeraldine PANI was added into 100 mL of $N$-methylpyrrolidone and refluxed with agitation for a certain period. Then, it was filtered to remove un-dissolved PANI. The PANI modified PAA membranes were obtained by depositing PANI on dry NaOH etched PAA membranes using a membrane casting method. Finally, the PANI modified PAA membranes were immersed in 1 mol · L$^{-1}$ HCl at 60 °C for 6 h and then dried.

Scanning electron microscopic (SEM) images were collected with a JEOL JSM-6700F scanning electron microscope. CAs were measured on a dataphysics OCA20 contact-angle system at ambient temperature. Each average CA was obtained by at five different positions. XPS was performed with a VG ESCALab 220I-XL X-ray photoelectron spectrometer (XPS) (VG Scientific Co.,) using Al Ka radiation (1486.6 eV). The typical four probe technique was employed for the determination of the dc conductivity (FX-1 type).

## 3. RESULTS AND DISCUSSION

Figure 1a shows the SEM images of the commercial obtained PAA membrane (provided from Whatman Co., England). The pore diameter ranges from 200 to 300 nm. The average pore diameter and pore density are 235 nm and 10$^{10}$ pores cm$^{-2}$, respectively. Figures 1(b)~(f) show the surfaces after erosion by NaOH solution. The external surface and the thin porous wall were partially dissolved and destroyed to fragments. At the same time, the bulk porous layers were pitted. After 3 to 5 min of etching time, the thin nano-cavity wall was etched enough to afford

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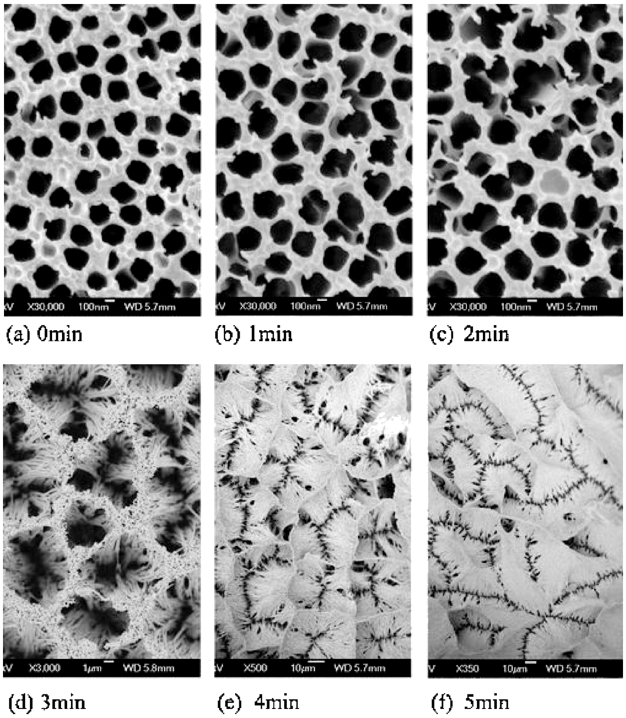


(a) 0min (b) 1min (c) 2min
(d) 3min (e) 4min (f) 5min

**Fig. 1.** SEM images of the PAA membranes pitted by 3 mol $L^{-1}$ NaOH solution for 0–5 min, respectively. The etching procedure is: 1.00 g of emeraldine PANI was added into 100 mL of *N*-methylpyrrolidone and reflux with agitation for a certain period. Then, it was filtered to remove un-dissolved PANI. The PANI modified PAA membranes were obtained by membrane casting method on dried NaOH etched PAA membranes.

$Al_2O_3$ nano-lines. When drying, the adjacent $Al_2O_3$ nano-lines shrunk together because of water surface tension, resulting in a special micro- and nanostructure (shown in Figs. 1(b)~(f)). The deeply pitted rupture structure of the bulk porous layer was developed, and the size of micro-cavity and the incline degree of cavity wall increased. After 6 min of etching, the PAA membrane became too fragile to be taken out from solution.

After etching, the samples were modified with PANI. As shown in Table I, the CA for water of a flat emeraldine PANI surface was $82.5 \pm 0.1°$, and the CAs of the PANI modified PAA membranes increased with etching time. This indicates that the surface hydrophobicity increased after being etched. When the etching time is longer than 4 min, the surfaces became super-hydrophobic. The CAs for the membranes of (e) and (f) were $151.5 \pm 1.5°$ (4 min) and $154.0 \pm 0.8°$ (5 min), respectively.

A theoretical consideration is always helpful to deepen our understanding of the hydrophobicity. The CAs could be expressed by Cassie–Baxter equation[9] (Eq. (1)). Here, $f_1$ and $f_2$ are the fraction of interface areas of water with PANI-modified PAA membrane and of air in the troughs, respectively. Thus, $f_1 \pm f_2 = 1$. The value of $f_2$ can indicate the surface roughness. The larger the value of $f_2$, the rougher the surface is. $\theta_r$ and $\theta$ are the CAs on the PANI-modified PAA membrane and the flat smooth PANI membrane, respectively. In this study, $\theta$ is $82.5 \pm 0.1°$. Therefore, $f_2$ can be calculated based on the measured $\theta_r$ values.

**Table I.** The contact angle (CA) for water of the NaOH etching PAA surface after being modified by PANI and the proportion of air ($f_2$).

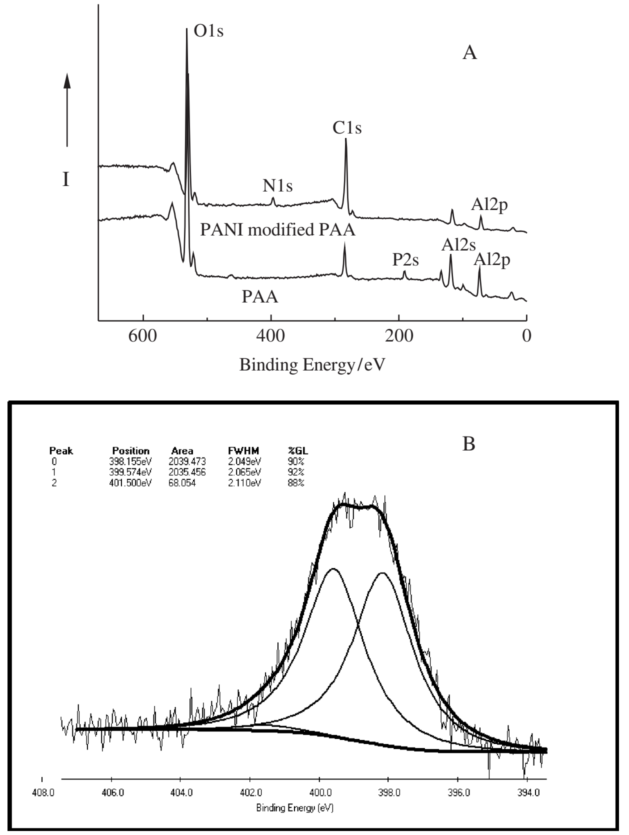
| Samples* | Contact angle for water/° | Proportion of air $f_2$ | Structure |
|---|---|---|---|
| PANI membrane | 82.5 ± 0.1 | | Smooth membrane |
| (a) | 135.0 ± 2.0 | 0.74 | Nano-cavity structure |
| (b) | 140.0 ± 0.7 | 0.79 | Nano-cavity structure, rougher than (a) |
| (c) | 140.5 ± 1.0 | 0.80 | Nano-cavity structure, rougher than (b) |
| (d) | 147.0 ± 1.5 | 0.86 | Micro- and nanostructure |
| (e) | 151.5 ± 1.5 | 0.89 | Micro- and nanostructure |
| (f) | 154.0 ± 0.8 | 0.91 | Micro- and nanostructure |

*Etching time for a, b, c, d, e, and f are 0, 1, 2, 3, 4, and 5 min, respectively.

$$\cos\theta_r = f_1\cos\theta - f_2 = (1 - f_2)\cos\theta - f_2 \tag{1}$$

$f_2$ for the as-obtained PAA membrane is 0.74 due to the presence of nano-cavity structure. And its $\theta$ angle ($135.0 \pm 2.0°$) is 52.5° higher than that of the smooth PANI membrane ($82.5 \pm 0.1°$). These results indicate that the nano-cavity structure may contribute greatly to the dramatically increased hydrophobicity. After the PAA membrane was etched by NaOH solution for 1 and 2 min, the roughness of the nano-cavity structure surface increased (Fig. 1(b) and (c)), and $f_2$ for the PANI modified PAA membrane increased to be 0.79 and 0.80, respectively. After the PAA membrane was etched by NaOH solution for 3 min, a micro- and nanostructure appeared. $\theta_r$ increased to $147.0 \pm 1.0°$, which can be attributed to the enhancement of surface roughness, indicated by $f_2$ with the high value of 0.86. When the etching time reached 4 min, the $\theta_r$ and $f_2$ increased to $151.5 \pm 1.5°$ and 0.89, respectively. If the etching time was further prolonged to 5 min, $\theta_r$ increased to $154.0 \pm 0.8°$.

Surface chemical composition is the other major factor contributing to surface hydrophobicity other than surface roughness. In the X-ray photoelectron spectra (XPS) (Fig. 2A), Al2p and Ols binding energies are 74.1 eV and 531.8 eV of the original PAA membrane. The appearance of the P2s peak may come from the residue of $H_3PO_4$ during the preparation of the PAA membrane. As for PANI modified PAA membrane, the N1s binding energy is 399.25 eV and its content is 3.52%. O1s Binding energy is 531.9 eV. And the Al2p binding energy is 73.8 eV, its content is 13.89%. This suggests that the surface of the PAA membrane was not totally covered by PANI. Further deconvolution result in Figure 2B shows that the nitrogen has 3 states, aniline nitrogen (–NH–) (399.5 eV), quinonimine nitrogen (–N=) (398.4 eV) and protonated nitrogen ($N^+$) (401.5 eV). And their contents are 40.91%, 50.09%,



| Peak | Position | Area | FWHM | %GL |
|---|---|---|---|---|
| 0 | 398.155eV | 2039.473 | 2.049eV | 90% |
| 1 | 399.574eV | 2035.456 | 2.065eV | 92% |
| 2 | 401.500eV | 68.054 | 2.110eV | 88% |

**Fig. 2.** XPS spectra of the PAA and PANI modified PAA membranes (A), N1s distribution by deconvolution (B).

and 2.4 × $10^{-3}$%, respectively. In other words, PANI are mainly emeraldine.

It is very interesting that after the PANI modified PAA membrane was immersed in HCl, a surface with both superhydrophobicity and high conductivity was obtained. Its CA for water was 155.0 ± 0.6°, as shown in Figure 3, and its conductivity is $8.8 \times 10^{-3}$ s $cm^{-1}$ measured by a typical four-probe technique. Note that the conductivity of the emeraldine PANI smooth membrane and the membrane (f) (i.e., PAA membrane after etching by NaOH for 5 min) are less than $10^{-8}$ s $cm^{-1}$. The XPS analysis in Figure 4 shows that content of aniline nitrogen (399.70 eV), quinonimine nitrogen (398.60 eV) and protonated nitrogen (401.80 eV) are 77.56%, 7.06%, and 15.39%, respectively, which increased the conductivity.

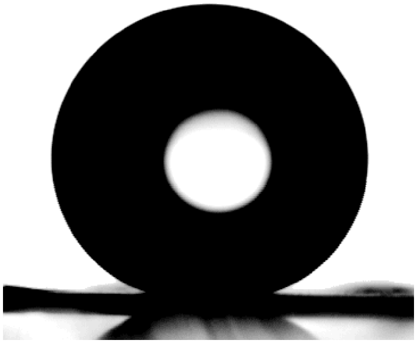
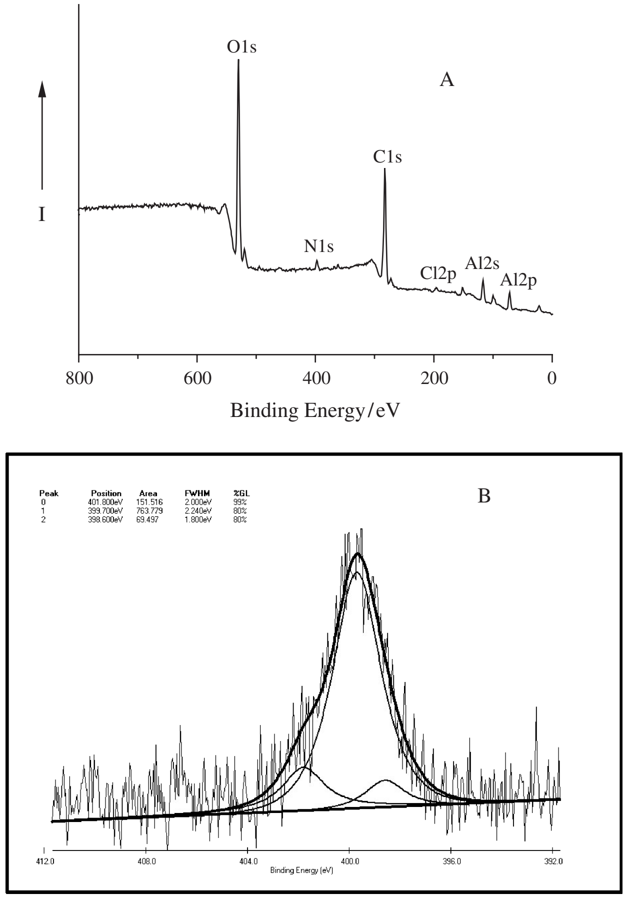


**Fig. 3.** Shape of water droplet on the dried PANI modified PAA membrane surface after being immersed in 1 mol $L^{-1}$ HCl solution at 60 °C for 6 h.



| Peak | Position | Area | FWHM | %GL |
|---|---|---|---|---|
| 0 | 401.800eV | 151.516 | 2.000eV | 99% |
| 1 | 399.700eV | 763.779 | 2.240eV | 80% |
| 2 | 398.600eV | 69.497 | 1.800eV | 80% |

**Fig. 4.** XPS spectra of the PANI modified PAA membrane after being immersed in HCl solution (A), N1s distribution by deconvolution (B).

## 4. SUMMARY

The present study provides a new route of using a conductive polymer (PANI) as a surface modification agent to afford super-hydrophobic surfaces. By a simple etching procedure, the surfaces of the as-obtained PAA membranes with appropriate roughness and micro- and nanostructure were obtained. Then, the surfaces were modified with PANI to afford to be super-hydrophobic. It is also interesting that after being immersed in HCl, the PANI modified PAA membranes became conductive and the superhydrophobicity was preserved. This method avoids using of the high cost and non-environmental friendly compounds. More importantly, the present study may offer a new approach to design surfaces with both desired wettability and functionality.

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