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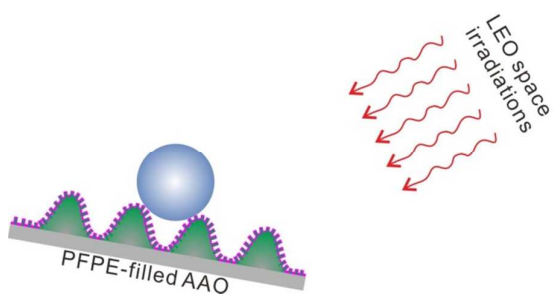
Perfluoropolyether infused porous anodic alumina keeps superhydrophobicity durably under simulated space irradiations at the low earth orbit (LEO).

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ARTICLE

Highly durable hydrophobicity in simulated space environment

Ruisheng Guo,[a,b] Haiyuan Hu,[a] Zhilu Liu,[a] Xiaolong Wang[*a] and Feng Zhou[*a]

By infusing perfluoropolyether lubricating liquids into hierarchical micro- and nano-structures, a highly durable hydrophobic material was obtained for resisting low earth orbit space irradiations, such as atom oxygen, ultraviolet, proton, and electron irradiations.

Introduction

Increasing bionic researches, inspired by many natural superhydrophobic surfaces, have developed enormous artificial superhydrophobic surfaces.[1-6] These surfaces could have extensive applications in self-cleaning, anti-fouling, anti-icing, drag reduction, and water/oil separation etc,[7, 8] which, however, are seriously hindered by their poor durability. Unlike natural plants, superhydrophobicity that can be preserved very well due to the unique regeneration ability of living species,[9] artificial surfaces could lose the superhydrophobicity permanently because of damages to either the rough structures or the low surface energy materials on the top surface. Especially for the latter, they can be damaged by mechanical wear, or decomposed due to sunlight. Recently, several methods have been employed to improve the resistance of artificial superhydrophobicity to environments, such as using anti-friction materials,[10, 11] easily repairable materials,[12-18] and controlled-release materials.[19-23]

However, durability of the superhydrophobicity could be still concerns when these surfaces are exposed to extremely rigorous environments like aerospace in low earth orbit (LEO), where plasma, light, and electromagnetic radiations (including atomic oxygen, ultraviolet, protons, and electrons) are extremely harsh toward almost all of the polymers used in spacecraft.[24, 25] Due to its high chemical reactivity and high impinging energy (~5 eV) when considering the very high relative velocity between spacecraft surface and atomic oxygen (AO), it can erode all kinds of organic materials. As a matter of fact, the monolayer of fluorocarbon polymers that are commonly used in artificial superhydrophobic surfaces could stand only seconds to AO irradiation before eroded completely.[26, 27] This may result in serious loss of superhydrophobicity or hydrophobicity of artificial materials. Therefore, developing durable hydrophobic surfaces under extremely rigorous space environment is a highly challenging task.

In this work, a new material to address above challenge is introduced using a facile fabrication method, *i.e.*, liquid perfluoropolyether (PFPE) fills up the micro- and nano-scale hierarchical structure of anodic aluminum oxide (AAO). PFPE

is commonly used as lubricant in aerospace vehicle because of its high stability with low volatility and high temperature resistance in space environment. Specially, it is liquid in room temperature with very low surface energy, thus can be conveniently imbued into the huge inner space of the hierarchical micro- and nano-scale structures. The cleverest moment of this material is that micro- and nano-scale structures can be as a reservoir to store liquid PFPE. Even though outmost PFPE molecules of PFPE-filled AAO are eroded by space irradiations, stored PFPE molecules in bottom gaps of AAO can creep and spread all over the top surface of AAO to keep the material hydrophobic. To verify this hypothesis, PFPE-filled AAO were conducted to experience various vacuum irradiation tests in simulated space environment, such as AO, ultraviolet (UV), proton, and electron irradiations. The exposed samples were subjected to surface morphology and chemical composition characterizations to investigate the effects of various irradiations.

Experimental

Materials and methodology

The micro- and nano- structure anodic alumina oxide was prepared by unconventional two-step anodization as the procedure reported in the literature.[28] Once ready, they were immersed into a 2.5% (v/v) PFPE (Sinopec Lubricant Company) solution in 1,1,2-trichlorotrifluoroethane (Sigma-Aldrich) for 24 h to load PFPE, followed by rinsing with acetone. Finally, PFPE-filled AAO were prepared by heating at 100°C for 60 min to completely remove the solvent remained in PFPE and promote molecular rearrangement. Two samples were fabricated as controlled experiments. One was prepared by sping-coating a droplet of pure PFPE liquid on silicon surface at 1000 rpm for 2 min; another was prepared by spin-coating PFPE solution on AAO surface at 3000 rpm for 60 s. Both controlled samples were treated by heating at 100 °C for 60 min in an oven. The PFPE-filled AAO were then put into chamber of a space environment simulation facility at Lanzhou Institute of Chemical Physics to conduct the AO irradiation at 4.0×10^{-3}

Pa. The flux of AO is 6.73×10^{15} atoms cm^{-2} s^{-1}. Exposure time of 0.5 h, 1.5 h, 2.5 h, 3.5 h and 5 h were carried out respectively to investigate the time independence of wettability of PFPE-filled AAO. Meantime, we also carried out other irradiations such as UV exposure, proton irradiation, and electron irradiation. UV exposure experiment was carried out under excimer light with wavelength of 200-450 nm under the pressure of 4.0×10^{-3} Pa using a mercury Xenon lamp, the intensity of which was determined by an UV monitor to be 15.8 mW cm^{-2}; proton irradiation experiment was conducted under the pressure of 3.0×10^{-3} Pa; for electron irradiation, the energy of the electron beams was 28 KeV and its power flux was 50 μA cm^{-2}. Please note that we label samples as irradiation-XXh according to the irradiation type, such as AO-0.5h represents the sample exposed to AO irradiation for 0.5 h.

Characterizations

Contact angles (CA) were acquired using a DSA-100 optical contact-angle meter (Kruss Company, Ltd, Germany) at ambient temperature (25 °C) by injecting 5 μL of testing liquids onto the samples, and the CA value was determined automatically using the Laplace–Young fitting algorithm. Average CA values were obtained by measuring the sample at five different positions, and images were captured with a digital camera (Sony, Ltd, Japan).The surface morphologies were observed using a field-emission scanning electron microscope (SEM, JSM-6701F, Japan) at 5-10 kV. The changes in the chemical structure of the PFPE-filled AAO were recorded by Fourier transform infrared spectra (FTIR) on a TENSOR 27 instrument (BRUKER, KBr disks for compounds and polymers, while ATR was used for modified surfaces). Chemical composition information were obtained by X-ray photoelectron spectroscopy (XPS), which was carried out on a PHI-5702 multi-functional spectrometer using Al Kα radiation and the binding energy were referenced to the C1s line at 284.6 eV from adventitious carbon.

Results and discussion

In order to investigate the wettability of PFPE modified AAO after AO irradiation, contact angles for water were measured. Before irradiation, the CA of PFPE-filled AAO was ~72 °when a 5 μL water droplet was dropped on its surface. Fig. 1a shows CA dependence on irradiation time and storing time after irradiation, from which it can be easily seen that the CA varied from 135°, 138°, 114°, 83°, to 0° when prolonging the irradiation time from 0.5 h, 1.5 h, 2.5 h, 3.5 h, to 5 h. However, the CA of all the exposed samples returned back to >130° surprisingly after being stored for 3 days at atmosphere, which was 138°, 139°, 149°, 137°, and 132°, respectively. Increasing stored time to 30 days and 130 days, corresponding CA increased at first, and decreased a little subsequently. In a word, regardless of how long PFPE-filled AAO were irradiated by AO, they always kept hydrophobic when being stored at atmosphere. Furthermore, we tested their repeatability by investigating if they can endure multiple cycles of AO exposure. Herein, heating and pumping were applied to speed up the healing of hydrophobicity. From Fig. 1b, we can see that PFPE-filled AAO remained excellent hydrophobicity (CA~139°) via several cyclic tests of irradiating-healing.

To probe the reason of CA changes of PFPE-filled AAO under AO irradiation, surface morphologies, chemical

structures, and chemical compositions were characterized by SEM, FTIR, and XPS before and after AO irradiation.
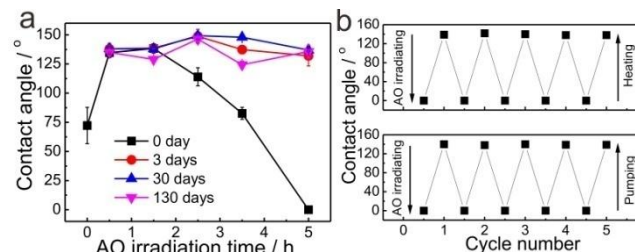

Fig. 1 Durable hydrophobicity of PFPE-filled AAO irradiated by AO irradiation. (a) Dependence of contact angle of water droplet on PFPE-filled AAO surface on exposure time and storing time before and after irradiation. (b) Repeatability of enhanced reversible transition between hydrophilicity and hydrophobicity by heating (top) and pumping (bottom) after irradiation. Different shape symbols represent the storing time at atmosphere after irradiation (square: 0 day; circle: 3 days; upper triangle: 10 days; lower triangle: 130 days).
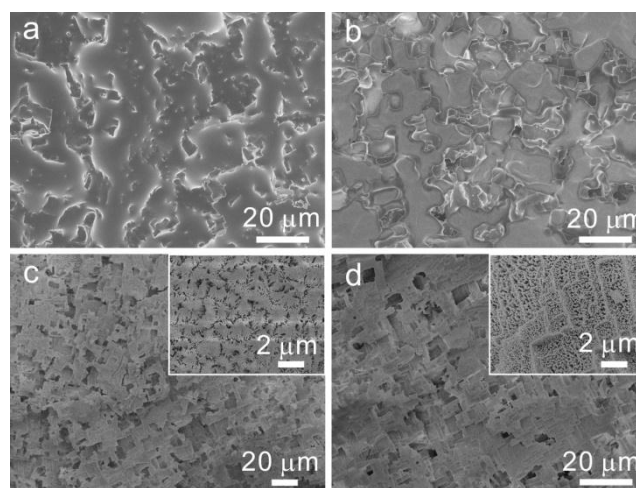

Fig. 2 SEM surface morphologies of PFPE-filled AAO before AO irradiation (a) and after irradiation for (b) 0.5 h, (c) 2.5 h, and (d) 5 h. The inset of (c) and (d) are corresponding magnified view.

Surface morphologies of PFPE-filled AAO are shown in Fig. 2a. It is obvious that PFPE completely covered the rough and hierarchical AAO surface. Although there are some rugged areas, the surface is relatively flat compared with bare AAO (Fig. S1). After AO irradiation, PFPE on the AAO surface was reduced obviously with increasing irradiation time, which is clearly shown in Fig. 2b-d in sequence corresponding samples irradiated for 0.5 h, 2.5 h and 5 h. The hierarchical AAO structures were recovered after irradiation for 2.5 h and 5 h, even nanowire structures can be seen obviously from the inset of Fig. 2c and 2d, compared with samples with shorter irradiation time of 0.5 h. We can conclude that the more irradiated time has the more exposure of the hierarchical structures.

The surface chemical structures before and after irradiation are shown in FTIR spectra from Fig. 3. Non-irradiation PFPE filled-AAO consisted of C-O-C stretching vibration mode at 981 cm^{-1} and 1121 cm^{-1}, CF stretching vibration mode at 1182 cm^{-1}, CF$_2$ stretching vibration mode at 1228 cm^{-1}, and CF$_3$ stretching vibration mode at 1306 cm^{-1}. All these peaks could be assigned to the PFPE molecule structure. While after AO irradiation, it is clear that intensity of CF$_2$ and CF$_3$ peaks

reduced seriously, and positions shifted to 1222 cm⁻¹ and 1297 cm⁻¹ (inset of Fig. 3) respectively. The reduction of intensity is attributed to the loss of PFPE by AO erosion and the hierarchical structure exposure because of the PFPE loss, which led to weak contact between sample and ATR probe of FTIR instrument during characterization. The reason of peak shift is unclear yet. It may be caused by large roughness of surface or other unknown materials.
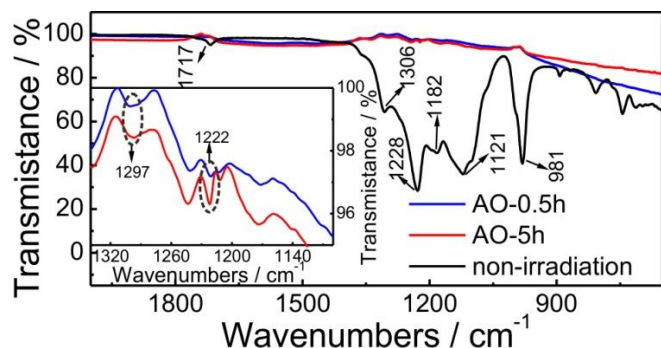

Fig. 3 FTIR spectra of PFPE-filled AAO before and after AO irradiation for 0.5 h and 5h. Inset: Zoom-in view of FTIR spectra of samples after AO irradiation from 1100 to 1340 cm⁻¹.
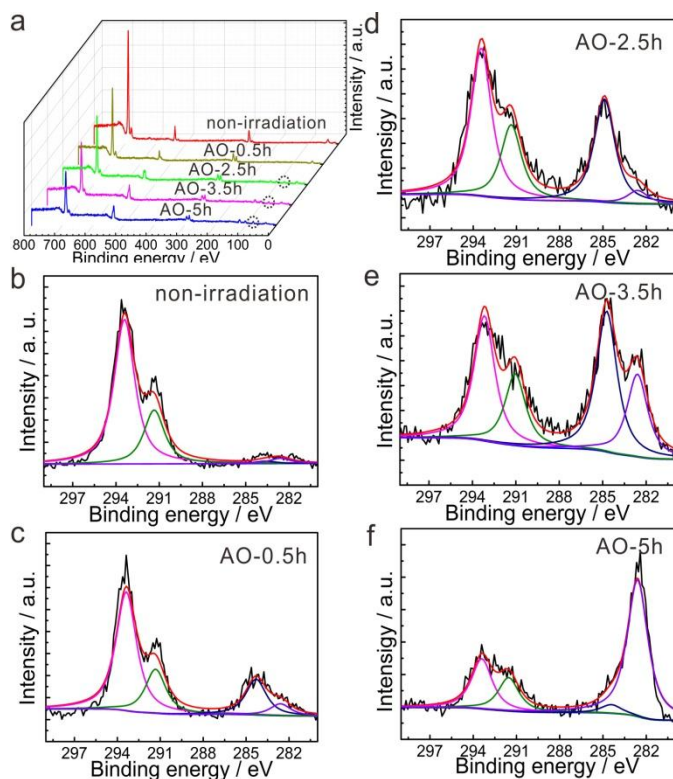

Fig. 4 XPS survey spectra (a) of PFPE-filled AAO before and after AO irradiating and storing for 10 days. C1s fine spectra of PFPE-filled AAO before irradiating (b), and after irradiating for 0.5 h (c), 2.5 h (d), 3.5 h (e), and 5 h (f). All irradiated samples were stored for 10 days.

The chemical compositions of PFPE-filled AAO before and after irradiation were measured by XPS (Fig. 4). Please note that the irradiated samples were stored for 10 days at atmosphere before XPS measurement. It can be found that all

samples included F, O, and C peaks. It is interesting that the samples with 2.5 h, 3.5 h, and 5 h of AO irradiation emerged Al peaks, which indicates that most of the outermost PFPE had been scissored and bottom Al_2O_3 had been exposed roundly with an increase of irradiation time. These results are consistent with previous SEM morphology change. The fine spectra of C1s can display some change information of chemical compositions from Fig. 4b-f. Before AO irradiation, there were strong C1s peaks localized at 293.4 eV and 291.4 eV, which are respectively attributed to CF_2-CF_2-O and CF_2-CF_2-CF_2 from PFPE,[29] and another two weaker peaks localized at 284.6 eV and 282.6 eV. After increasing irradiation time from 0.5 h to 5 h, intensity of CF_2-CF_2-O and CF_2-CF_2-CF_2 decreased gradually due to erosion of main chain backbones. However, all samples had CF_2-CF_2-O and CF_2-CF_2-CF_2 signals, indicating that PFPE molecules still exist on the sample surfaces. Other two peaks arose obviously at binding energy of 284.6 eV and 282.6 eV, which may result from C-C (C-H) bond and Al-O-C (or Al-C-like species) respectively.[30-32] Peak intensity of AO-0.5h to AO-2.5h and AO-3.5h located at 284.6 eV went up while that of AO-5h went down. Going up may be because plenty of dangling bonds formed by breaking of carbon chain absorb lots of water or carbonaceous molecules at atmosphere or react to form a cross-linked polymer on surface; going down is because 5 h of AO irradiation clear surface PFPE completely leading to much loss of active sites and less formation of C-C (C-H). Al-O-C (or Al-C-like species) located at 282.6 eV could be formed due to the annealing procedure at 100 °C. There have been literatures reporting that Al_2O_3 promoted PFPE decomposition from C-O bonds of C-C-O as a lewis acid at above ~200 °C.[33,34] It is deduced that the decomposition products (such as C-C- or -O-C-C) of PFPE may react with active Al_2O_3, forming C-C-Al or Al-O-C at local areas (temperature could over 200 °C due to local overheating). Its intensity increased relatively with irradiation time is due to reduce of PFPE molecules. All these indicate that AO irradiation mainly causes the breaking of PFPE main carbon chains.
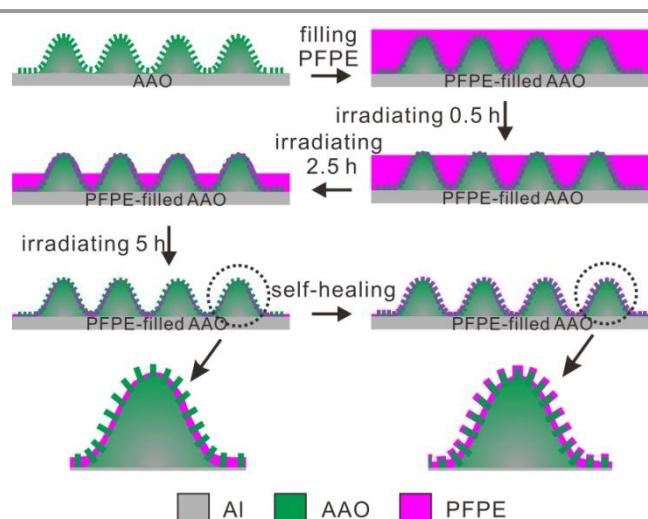

Fig. 5 Schematic illustration of surface changes of PFPE-filled AAO via AO irradiation.

It is well known that hydrophobic surface is composed of rough structure and low surface energy material. The loss or recover of hydrophobicity can be derived from their damages or recover. Combining previous mentioned SEM morphologies,

FTIR spectra analysis, and XPS composition characterization, we can effectively deduce wettability behaviors of PFPE-filled AAO during AO irradiation with the schematic illustration of Fig. 5. The hierarchical micro- and nano-structure AAO was immersed into PFPE solution, making PFPE solution fill up the hierarchical structures and forming a thick and plain film on the top surface. Although there were plenty of CF_2 groups, the flat surface exhibited hydrophilic behavior with CA of ~72°, which is just like the spinning coated PFPE film on Si-wafer (~77°) in Fig. S2. After AO irradiation with a kinetic energy of about 5 eV, it caused a pure physical sputtering of the surface atoms in the absence of any chemical changes. The PFPE main carbon chain backbones were scissored and lots of small molecules volatilized (CF_2O, CF_2, and CF_3) at the same time, which resulted in PFPE film getting thinner and thinner gradually with irradiation time. After irradiated for 0.5 h, some PFPE were removed resulting in the surface getting rougher so that the CA value increased to 135°. With increasing irradiation time to 2.5 h, PFPE main carbon chains were further reduced seriously, which led to exposures of few protrusions of hierarchical micro- and nano-structures of AAO with oxygen-containing hydrophilic groups due to AO erosion. So the water contact angle decreased to 114° slightly compared to 135° of AO-0.5h. Further increasing irradiation time to 5 h, PFPE molecules on the surface where AO can arrive were removed completely, so the surface became completely wettable. However, it is very surprising that AO-2.5h and AO-5h samples recovered their hydrophobicity after stored at atmosphere for 3 days, and the CA could recover to 149° and 132°, respectively. It may be that AO exposure hadn't significant impact on underlying PFPE that were deeply embedded into bottom gap of AAO, therefore residue PFPE molecules could creep out from bottom and spread all over the hierarchical surface at atmosphere, forming PFPE monolayer and producing hydrophobic surface again, which is agree well with XPS spectra of AO-2.5 and AO-5h. In order to further demonstrate PFPE monolayer on AAO surface can play a role of repulsing water, we prepared PFPE-coated AAO surface by spin-coating and got the CA~145° (Fig. S2). Above deduction can also be verified by cyclic tests of irradiating-healing (by pumping and heating) shown in Fig. 1b. Low pressure caused by pumping could result in quick molecule diffusion due to an increase of molecular free path, so recovering time of hydrophobicity was shortened from several days to less than 5 h. For heating treatment, on the one hand, high temperature could help PFPE molecules to fast diffuse from AAO bottom to AAO top surface; on the other hand, high temperature could increasingly make PFPE molecules to rearrange on AAO surface. So recovering time was also shortened from several days to ~3 h.

Besides the effect of AO irradiation on the wettability of PFPE-filled AAO, we also investigated the effects of other LEO space irradiations including UV, proton, and electron irradiations. It is found that PFPE-filled AAO can keep hydrophobicity with the three types of irradiations to some extent. Fig. 6a shows the wettability changed under UV irradiation for 4 h, 6 h, 8 h, 10 h, and 12 h. It is clearly showed that CA increased with irradiation time from 117° to 127°, 127°, 132°, and 133°. The CA values of samples stored at atmosphere for 3, and 30 days after irradiation were measured to investigate the hydrophobic durability, their CA had a little bit of changes as compared with that of non-stored samples. By proton irradiation, water CA values were 129° for 3 min, 134° for 6 min, 127° for 9 min, and 132° for 12 min. After being stored for 3 or 10 days, all these samples experienced some rises of

CA ranging from 4° to 13°. By electron irradiation, the CA values had a rough increase from 104° to 146°, corresponding irradiation time from 5 to 25 min. Similarly, the CA arrived at above 120° even 146° after stored at atmosphere for 3 or 10 days. For both proton and electron irradiations, less than 30 min of irradiation time were selected. This is because they possess very high energy to corrode PFPE molecules comparing with AO irradiation. During even short time irradiation, a plenty of volatile molecules containing fluorine can accumulate and absorb onto vacuum chamber, resulting in chamber contamination. This can be verified by observing that the vacuum pressure rapidly increased from 10^{-3} Pa to 10^{-2} Pa within 30 min.
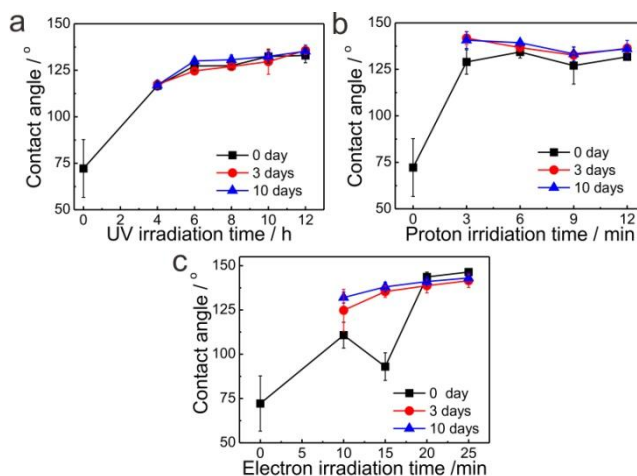

Fig. 6 Durable hydrophobic property of PFPE-filled AAO via UV, proton, and electron irradiations. (a) CA of PFPE-filled AAO before and after UV irradiation for 4 h, 6 h, 8 h, 10 h, and 12 h; CA of samples stored at atmosphere for 3 and 10 days after irradiation. (b) CA of samples before and after proton irradiation for 3 min, 6 min, 9 min, and 12 min; CA of samples stored at atmosphere for 3 and 10 days after irradiation. (c) CA of PFPE-filled AAO before and after electron irradiation for 10 min, 15 min, 20 min, and 25 min; CA of samples stored at atmosphere for 3 and 10 days after irradiation. (square: 0 day; circle: 3 days; triangle: 10 days)

To investigate the hydrophobic mechanism, surface morphologies of PFPE-filled AAO after UV, proton, and electron irradiations were characterized by SEM. For UV irradiation, surface morphologies of samples irradiated for 6 h and 12 h are shown in Fig. 7 a(i) and (ii). It can be seen that chemical materials still remained on AAO surface even though 12 h of irradiation, which may be due to PFPE molecule crosslinking while less being etched, so the surface always kept hydrophobicity. This can be evidenced by FITR spectrum of samples irradiated for 6 h and 12 h (Fig. 8). Their peak positions and intensity are similar to non-irradiation sample. For proton and electron irradiation, surface morphologies of samples can be seen in Fig. 7 b and c. All surface micro- and nano-structures of AAO were clearly observed, which are similar to pristine AAO structures, indicating that PFPE polymer on surface were almost removed completely even rough experiencing very short irradiation time of 3 min (proton) and 10 min (electron). It is deduced that electron or proton induced FPPE decomposition. However, irradiated samples were found always hydrophobic, which is different from atomic oxygen irradiation ones. This was attributed to dissociative fluorine species absorbing onto sample surface during irradiation, for which there is a above mentioned side witness

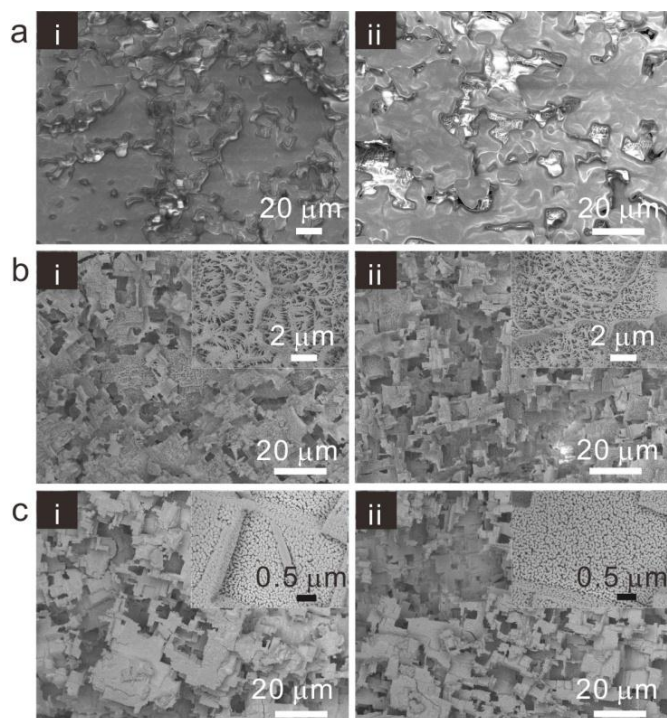by observing that the vacuum pressure rapidly increased from 10^{-3} Pa to 10^{-2} Pa within 30 min.

Fig. 7 SEM morphologies of PFPE-filled AAO irradiated by UV irradiation for 6 h (a (i)) and 12 h (a (ii)), proton irradiation for 3 min (b (i)) and 9 min (b (ii)), and electron irradiation for 10 min (c (i)) and 25 min (c (ii)).
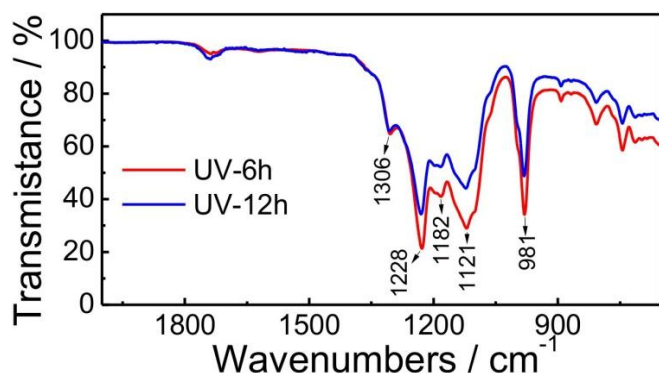

Fig. 8 FTIR spectra of PFPE-filled AAO after UV irradiation for 6 h and 12 h.

Conclusions

In conclusion, we developed a highly durable hydrophobic surface by using liquid perfluropolymer PFPE, usually used as lubricant in space aircraft, to fill up hierarchical micro- and nano-scale AAO. This material, PFPE-filled AAO, always kept hydrophobic no matter how long it experienced AO irradiation in simulated space. By SEM, FTIR, and XPS characterization and analysis, we knew that PFPE molecules with low surface energy always remains on AAO surface because: 1) short time irradiation can't completely clear PFPE molecules; 2) long time irradiation can remove PFPE molecules on sample surface, but PFPE embedded in AAO bottom will diffuse to AAO surface at

atmosphere. We also found that PFPE-filled AAO could keep hydrophobicity via other simulated space irradiation, such as UV, proton, and electron irradiations independently. Due to especially durable hydrophobicity, we believe that PFPE-filled AAO can be applied in some special environment. Simulated experiments of LEO space irradiations are accelerated tests, the irradiation dose are far more than that of real LEO space irradiation;[27,35,36] the vacuum degree which influences recovering speed of hydrophobicity is very lower than that of real LEO space. So we think it is possible that a balance may be kept between irradiation damage and self-healing of hydrophobicity in LEO space. Furthermore, If not being put on LEO space environment, we think the PFPE-filled AAO could also keep hydrophobic in special environment, such as plasma irradiation (similar to AO irradiation) and mechanical wear (if surface chemical is damaged, embed PFPE would diffuse onto top surface to recover hydrophobicity) and so on. Finally, we predict that other simple materials with similar both AAO structure and low surface energy chemical can be easily fabricated and applied in special environment.

Acknowledgements

Notes and references

^{a}State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China. E-mail: wangxl@licp.cas.cn; zhouf@licp.cas.cn.
^{b}University of Chinese Academy of Sciences, Beijing, 100049, P. R. China.
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experimental details, SEM images, photographs. See

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