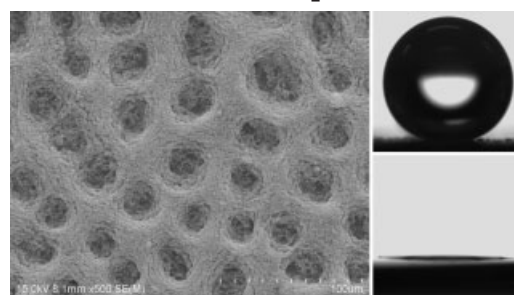


Hierarchical Pore Structures Fabricated by Electron Irradiation of Silicone Grease and their Applications to Superhydrophobic and Superhydrophilic Films^a

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Unique hierarchical pore structures were fabricated by simply irradiating an electron beam onto silicone grease films. The hierarchical pore structures consisted of micrometer-sized pores and macroporous walls. Due to the high surface roughness, the hierarchical pore structures exhibited both superhydrophobicity with a water contact angle (CA) of 170° and superhydrophilicity with an extremely low water CA of 3° after the chemical treatment of the surfaces. In addition to the hierarchical pore structures, sponge-like pore structures were also fabricated by the electron irradiation of silicone grease films.



Introduction

Lotus leaves have a strong superhydrophobicity with a water contact angle (CA) higher than 150° and a sliding

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angle (SA) of less than 10°, resulting in a self-cleaning effect that removes contamination and dirt on their surfaces.^[1] It has been revealed that the interesting self-cleaning effect of a lotus leaf can be attributed to the hierarchically combined microstructure and nanostructure and a low surface energy material on the surface. Hierarchical micro/nanostructures supply the high surface roughness that is necessary for superhydrophobicity. The effect of surface roughness on the wettability can be described by the Wenzel model,^[1a] which predicts that a hydrophobic surface (CA > 90°) becomes more hydrophobic and a hydrophilic surface (CA < 90°) becomes more hydrophilic as the surface roughness increases. Consequently, hierarchical micro/nanostructures can also induce superhydrophilicity as well as superhydrophobicity. Recently, various hierarchical micro/nanostructures have been synthesized for application in superhydrophobic and superhydrophilic surfaces, including microsphere/nanofiber composite films,^[2] a micro/nano binary colloid

assembly,^[3] nanoparticles on microstructured polymers,^[4] microparticles comprising nanorods or nanoparticles^[5] and hierarchical micro/nanodendrites.^[6]

Elastomeric polydimethylsiloxane (PDMS) has been widely used in many scientific and industrial fields, such as soft lithography, nano-imprinting, microfluidic devices, and anti-contamination coating materials, because of its attractive physical and chemical properties.^[7–9] PDMS has a slightly hydrophobic property with a water CA of around 105°; however, the wettability can be transformed into hydrophilicity by the treatment of the surface with ultraviolet (UV) light or plasma. If PDMS is exposed to UV light or plasma, a silica-like layer is formed on the PDMS surface due to the chemical decomposition of PDMS.^[10] This can lead to changes in the wettability of the PDMS surface^[10] and induce wave-like microstructures or nanostructures.^[11] In addition, we found that hierarchical tree-like nanostructures could be synthesized by irradiating an electron beam onto PDMS.^[12] The main difference between electron irradiation and UV or plasma irradiation is the penetration depth of the radiation into the material. If a material is exposed to UV and plasma, only the near surface region (<1 μm) of the material is affected, while energetic electrons can penetrate much deeper regions of the materials. As an example, the penetration depth of 50 keV electrons for PDMS is ca. 40 μm. Thus, if a thin film with a thickness less than a few tens of μm is irradiated with an electron beam, the chemical structures of the whole film can be completely changed by the electron irradiation.

Here we present a facile route to fabricate hierarchical pore structures, which consist of micrometer-sized pores and macroporous walls, by the electron irradiation of silicone grease that is a mixture of organic PDMS and inorganic silica nanoparticles. Hierarchical nanoporous structures combined with macropores and mesopores have been synthesized in several ways;^[13] however, the hierarchical micro/nanopore structures synthesized in this study are quite unique. The fabricated hierarchical pore structures have very high surface roughnesses and thus they exhibit two extreme water wettabilities of superhydrophobicity (water CA > 170° and SA < 3°) and superhydrophilicity (water CA < 3°) after proper chemical treatments.

Experimental Part

PDMS (\bar{M}_w : 300 000 g · mol⁻¹, Shin-Etsu Chemical Co., KF-96H) and silicone grease (Dow Corning high vacuum grease) composed of PDMS (\bar{M}_w : 380 000 g · mol⁻¹), silica nanoparticles (7–13 wt.%) and DMS monomer (7–13 wt.%), were used as the precursor materials. PDMS and silicone grease films were prepared by casting precursor materials onto a silicon (100) substrate

(20 mm × 20 mm) with various thicknesses from <1 μm to ≈50 μm. The prepared films were subsequently irradiated with an electron beam generated from an electron gun.^[12,14] The energy of an electron beam irradiating the films was 50 keV, the beam current density was 30 μA · cm⁻² and the beam diameter was around 20 mm. The total fluence of an electron beam irradiating the samples was varied from 1.1 × 10¹⁷ cm⁻² to 2.7 × 10¹⁸ cm⁻² by changing the irradiation time. The irradiating process was carried out at ambient temperature in a vacuum chamber under a pressure of less than 2 × 10⁻⁵ Torr.

After the electron irradiation, the morphologies of the electron-irradiated films were characterized with a field emission scanning electron microscope (FESEM, Hitachi S-4800). In addition, the in situ electron irradiation experiments were also performed using FESEM (Hitachi S-4300, beam energy: 15 keV) and the morphology changes during the electron irradiation were recorded with a CCD camera. The chemical composition of the films was characterized with X-ray photoelectron spectroscopy (XPS) using Mg and Al K α X-ray source in a SIGMA PROBE (Thermo VG) spectrometer. The XPS spectra were curve-fitted with a mixed Gaussian-Lorentzian shape using XPSPEAK analysis software.^[15] A Shirley function was used to remove the background prior to curve fitting. All the XPS spectra were charge compensated to C 1s at 284.6 eV.^[16]

The surfaces of the electron-irradiated films were chemically modified to get superhydrophobicity or superhydrophilicity. For superhydrophobicity, the irradiated films were treated with a low surface energy material of fluorosilane ((heptadecafluoro-1,1,2,2-tetrahydrodecyl) trichlorosilane) (Alfa Aesar); the samples were immersed in a hexane solution of 20 × 10⁻³ M fluorosilane for 30 min and dried at room temperature. For superhydrophilicity, a high surface energy material named D-0,^[17] which is a silica and titania based hybrid polymer fully functionalized with SO₃⁻Na⁺ groups, in an ethanol solution was spin-coated on the surfaces of electron-irradiated films, and was then dried in a vacuum oven at 50 °C for 12 h and subsequently at 100 °C for 3 h. The wetting properties of the film were analyzed using water CA and SA measured with a CA measurement system (KRÜSS, GSA10). The volume of the water drop used for the CA and SA measurements was 4 μL.

Results and Discussion

The silicone grease films were colorless but exhibited a black color after electron irradiation. Figure 1 shows typical FESEM images of the silicone grease films before and after electron irradiation. The surface of the pristine silicone film was flat (Figure 1(a)) and the thickness of the film was ≈10 μm. Interestingly, however, the flat surface turned into a rough surface with a hierarchical pore structure after electron irradiation at a fluence of 1.3 × 10¹⁸ cm⁻². The hierarchical pore structure consisted of micrometer-sized pores with diameters of 10–20 μm and macroporous walls with a pore size of 50–150 nm (Figure 1(b),1(c)). The macroporous walls comprised an aggregate of irregular nanoparticles of 30–70 nm in size

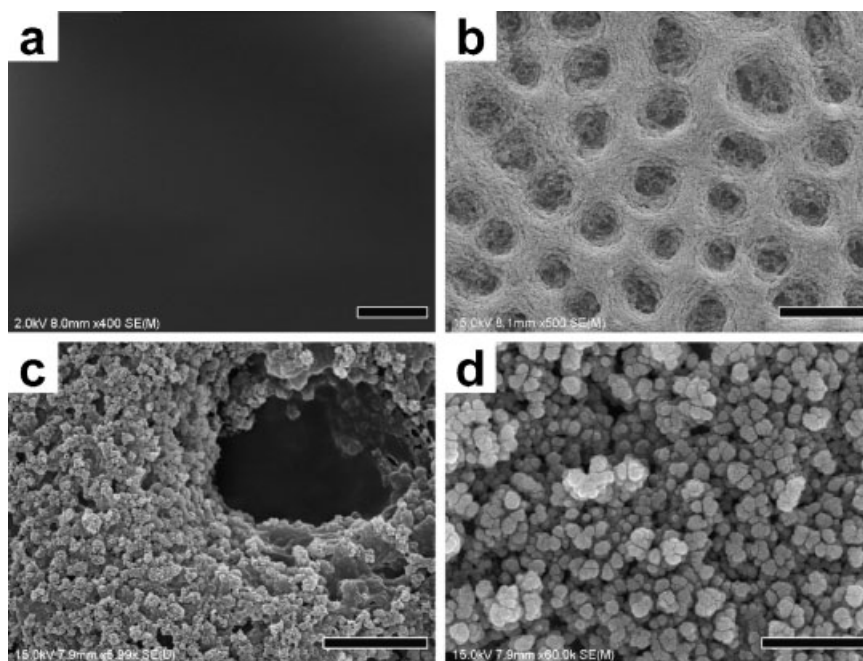


Figure 1. FESEM images of pristine and irradiated silicone grease films: (a) surface of a pristine silicone grease film; (b) hierarchical pore structures formed from an electron-irradiated silicone grease film; (c) magnified image of (b), showing micrometer-sized hole and the wall consisting of nanoparticles; (d) magnified image of macroporous wall. Scale bars are 50 μm for (a) and (b), 5 μm for (c) and 500 nm for (d).

and the macropores were formed between the nanoparticles (Figure 1(d)).

For comparison, we irradiated electron beams onto pure PDMS films and investigated changes in the morphology. The PDMS film thickness was about 10 μm and all the experimental parameters were the same as those used for the silicone grease films. In this case, no pores were formed on the surface and instead the soft and viscous polymeric film turned into a hard and brittle film after electron irradiation (see Supporting Information, Figure S1(a)). Many cracks were formed and the cracking occurred throughout the thickness of the film. XPS analysis indicated that the irradiated PDMS films contained silicon (Si), carbon (C) and oxygen (O), like the pristine PDMS films (Figure S2). However, the relative atomic ratio of O to Si increased, while the ratio of C to Si decreased. Furthermore, the peak position of Si 2p shifted from the pristine value of 102.1 eV to 103.1 eV, indicating that the chemical structure of the polymeric PDMS was transformed into inorganic silica-like structures or oxygen-rich silicon oxycarbide (see details in Figure S2). If PDMS with a repeating unit of $-\text{Si}(\text{CH}_3)_2-\text{O}-$ is irradiated with an electron beam, the molecular bonds of the polymer are broken by the energetic electrons. Generally, Si-CH₃ and C-H bonds are more easily broken than other molecular bonds and hence volatile products such as hydrocarbon and hydrogen molecules are generated, which are then removed from

the polymer into the vacuum environment.^[12] Due to the bond breakage, new chemical products are also formed under the irradiation.^[18] It has been reported that PDMS, upon electron irradiation, is transformed into silicon oxycarbide $\text{SiO}_x\text{C}_{4-x}$ ($0 \leq x \leq 4$) with different ratios between Si-O and Si-C bonds.^[12] Since the Si-C bond is more easily cleaved than the Si-O bond by the irradiation,^[12,19] the relative ratio of Si-O bonds to Si-C bonds increases with increasing electron fluence. As a result, after a high fluence of electron irradiation, the irradiated PDMS becomes a silica-like material or oxygen-rich silicon oxycarbide.^[10b,16,20] While viscous PDMS is converted to a hard silica-like material by the electron irradiation, volume shrinkage occurs.

Note that the conversion occurs due to the removal of the volatile products and that the density of silica is almost two times higher than that of PDMS. Figure S1(b) clearly demonstrates the volume shrinkage

phenomenon of PDMS under electron irradiation. When a localized rectangular region of the PDMS was selectively irradiated with an electron beam, the height of only the irradiated PDMS region was reduced. If a whole film was electron irradiated, large tensile stress was induced throughout the film because of the volume shrinkage, leading to the formation of cracks on the hard silica-like structures, as shown in Figure S1(a).

Unlike the pure PDMS film, the silicone grease film was a mixture of PDMS, DMS monomer and silica nanoparticles, and evolved into hierarchical pore structures under the electron irradiation. The formation process of the porous structure was more clearly observed by in situ electron irradiation experiments. Localized regions (500 $\mu\text{m} \times 500 \mu\text{m}$) of silicone grease films with a thickness of around 10 μm were irradiated with an electron beam generated from a SEM, which allowed in situ observation of the morphology changes during irradiation. If a pure PDMS film was locally irradiated with an electron beam, the irradiated region contracted and transformed into a silica-like material (Figure S1(b)). However, as displayed in Figure 2 and Figure S3, such a simple volume contraction did not occur when the silicone grease film was electron irradiated. Instead, bubbles were formed inside the irradiated films and these burst to form micrometer-sized pores on the surface, while the bubbles were removed into the vacuum environment (Figure S3). We believe that the

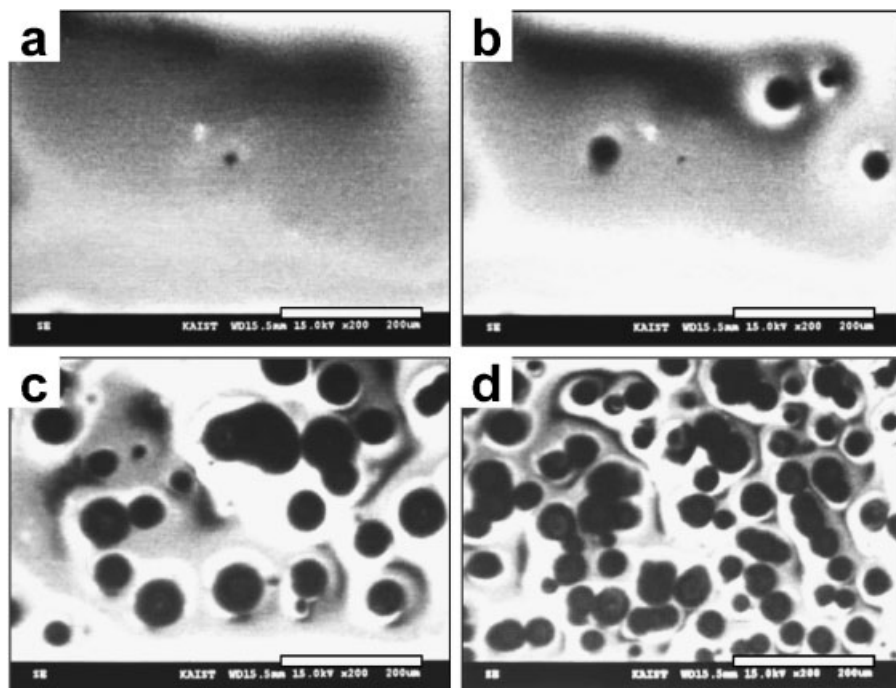


Figure 2. Images captured during the in situ electron irradiation experiment at different irradiation times: (a) 1 s; (b) 3 s; (c) 60 s; (d) 360 s. The irradiating beam current was around $1 \mu\text{A} \cdot \text{cm}^{-2}$. Scale bars are 200 μm .

bubbles were formed by volatile species, such as hydrogen and hydrocarbon gas,^[14] which were generated by the decomposition of PDMS or DMS inside the silicone grease film. Note that if a silicone grease film is irradiated with an electron beam, organic PDMS and DMS components in the film decompose, whereas the inorganic silica nanoparticles embedded in PDMS remain almost intact. As the electron fluence increases, decomposition of PDMS in the silicone grease film continues and accordingly the number of pores produced on the film surface increases (Figure 2). Furthermore, the electron beam decomposes the organic material remaining between the pores, leaving silica nanoparticles, and thus macroporous walls are formed. As a result, hierarchical pore structures consisting of micrometer-sized pores and macroporous walls that are mainly composed of silica nanoparticles are fabricated. XPS spectra also identified that silica was the main component of the electron-irradiated silicone grease film (Figure S4).

The experimental results revealed that the thickness of the precursor film was a key parameter affecting the morphology of the electron-irradiated film. The hierarchical pore structures were formed only when the film thickness was between 7 μm and 15 μm . If the film thickness was less than 2 μm , another interesting pore structure, a sponge-like pore structure, which consisted of only silica nanoparticles and macropores, was created (Figure 3). Similar sponge-like pore structures have been synthesized by other methods.^[21] The in situ electron

irradiation experiments identified that no micrometer-sized pores were formed if such a thin silicone grease film was electron irradiated. This is probably because volatile species produced by the decomposition of organic materials were not trapped inside the film but were easily removed into the vacuum environment because of the thin film thickness. Consequently, bubbles and the resultant micrometer-sized pores were not generated. In this case, organic materials in the film were steadily decomposed by the electron irradiation and only silica nanoparticles embedded in the organic materials remained, resulting in the sponge-like pore structures. The morphology of the sponge-like pore structure was similar to that of the macroporous wall of the hierarchical pore structure. On the contrary, when the thickness of the film was larger than 30 μm ,

several micrometer-sized pores were randomly formed and nanoparticles were rarely found on the surface (Figure S5). In situ irradiation experiments of the thick films showed that pre-formed pores tended to disappear because viscous polymeric materials surrounding the pores flew into the pores. However, if the film thickness was around 10 μm , pores that were once formed on the film surface could survive, suggesting that the amount of polymeric material was not sufficient to completely fill the pores. These results show that different morphologies can be produced using the electron irradiation technique just by changing the film thickness.

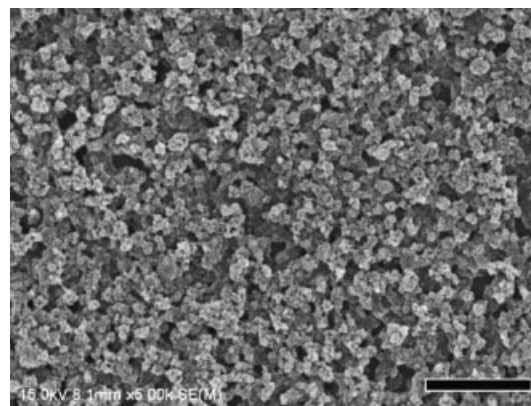


Figure 3. FESEM image of the sponge-like pore structure. Scale bar is 5 μm .

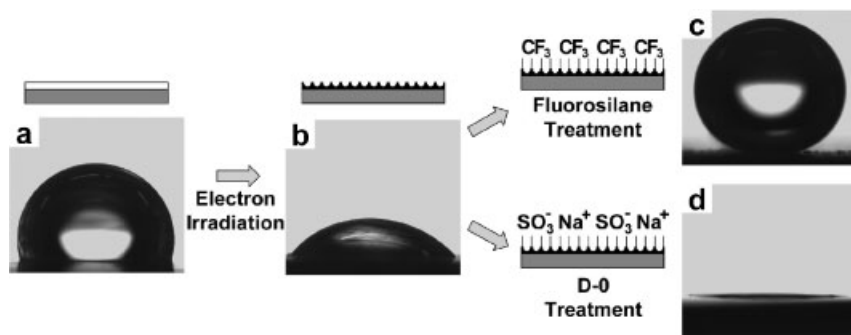


Figure 4. Water contact angles of the silicone grease films measured (a) before the electron irradiation, (b) after the electron irradiation, (c) after the surface treatment of the irradiated film with fluorosilane, (d) after the surface treatment of the irradiated film with D-0.

The irradiated silicone grease films with hierarchical pore structures can provide high enough surface roughness to induce both superhydrophobicity and superhydrophilicity. The surface wettabilities of the films before the electron irradiation and after the electron irradiation were investigated by water CAs and SAs. The water CA of the pristine silicone grease film was ca. 105° (Figure 4(a)), exhibiting hydrophobicity. However, after the electron irradiation, the water CA of the film with the hierarchical pore structures was reduced to 48° (Figure 4(b)), indicating that the film was transformed from hydrophobic into hydrophilic. Due to the formation of the hierarchical pore structure, the surface roughness of the electron-irradiated film was dramatically increased compared to the pristine film. Therefore, if the chemical structure of the film was not changed under the electron irradiation, the electron-irradiated film should be more hydrophobic than the pristine film. However, since the electron irradiation converted silicone grease to silica-like material, a reverse behavior was observed, that is, the electron-irradiated film became hydrophilic.

For application to superhydrophobicity and superhydrophilicity, the surface of the electron-irradiated film with a hierarchical pore structure was chemically treated with a low surface energy material (fluorosilane) and a high surface energy material (D-0), respectively, as described in the *Experimental Part*. After the surface treatment, the electron-irradiated films exhibited dramatic changes in wettability. When the surface of the electron-irradiated film was treated with fluorosilane, the water CA of the film was strikingly increased from 48° to 170° (Figure 4(c)), reflecting that the surface was changed from hydrophilic to superhydrophobic. Additionally, the measured advancing and receding CAs of the fluorosilane-treated film were $169 \pm 1^\circ$ and $166 \pm 1^\circ$ (Figure S6), respectively, suggesting a very low CA hysteresis and a SA of about 3° , which was further identified by the measurements (Figure S7). In the process of CA measurements, we found it difficult to add a water droplet to the fabricated surface, suggesting that the surface has very

low adhesive force. The presence of superhydrophobicity with such a low SA and the difficulty in dropping water on the surface provide strong evidence of the lotus effect for the fabricated surface with the hierarchically combined micro/nanostructure. On the contrary, when the surface of the electron-irradiated films was treated with D-0, the water CA of the films was dramatically decreased to 3° (Figure 4(d)), indicating that the surface took on superhydrophilic properties. Therefore, these experimental results demonstrate that the electron-irradiated silicone

grease films with a hierarchical pore structure can be controlled to have extremely opposite wettability, superhydrophobicity or superhydrophilicity, through proper surface treatment.

Conclusion

A novel strategy to fabricate unique hierarchical pore structures that consist of micrometer-sized pores and macroporous walls has been presented. The hierarchical pore structure was easily fabricated by irradiating an electron beam onto a silicone grease film. Due to the high surface roughness, the electron-irradiated films with hierarchical pore structures could show both superhydrophobicity and superhydrophilicity after the corresponding chemical treatment of the surface. The electron irradiation approach is a parallel process to simultaneously change both the morphology and the chemical structures of the irradiated films, allowing synthesis of large area hierarchical pore structures by increasing the electron irradiation area. In addition to the superhydrophobic and superhydrophilic films, we believe that the hierarchical pore structures have potential applications in catalysis, gas storage and biochemical sensors.^[22]

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