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Large-Area Fabrication of Micro/Nano Hierarchical Structure by Electron Irradiation and Its Application to Superhydrophobic Surface

Eun Je Lee, Sung Oh Cho*
Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea
**Corresponding author: Socho@kaist.ac.kr*

1. Introduction

Lotus leaves have a strong superhydrophobicity with a water contact angle (CA) higher than 150^o and a sliding angle (SA) less than 10^o, resulting in the self-cleaning effect that removes contamination and dirt on their surfaces [1,2]. It has been revealed that the interesting self-cleaning effect of a lotus leaf is attributed to the hierarchically combined micro- and nano-structure and a low surface-energy material on the surface. Micro/Nano hierarchical structures supply high surface roughness that is necessary for the 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^o) becomes more hydrophobic as the surface roughness increases. Consequently, micro/nano hierarchical structures can induce superhydrophobicity.

Recently, various mechanical and chemical methods, including molding, plasma etching, self-assembly, and electrochemical methods [3-6], have been developed for fabricating superhydrophobic surfaces. However, mechanical methods are time-consuming and expensive for large-area fabrication. On the other hand, Chemical methods have complicated processes in many cases.

Here we present a facile route to fabricate large-area superhydrophobic surface using micro/nano hierarchical structure produced by electron irradiation on organic/inorganic composite film.

2. Methods and Results

2.1 Sample preparation

Poly(methyl methacrylate) (PMMA) and silicone grease were used as a precursor material. At first, PMMA colloidal solution (60 wt %) was prepared with PMMA microsphere (Soken, 20 μm in diameter) powder and ethanol. It was spin-coated on the silicon substrate (4 inch in diameter) at 700 rpm for 1 minute. After that, silicone grease solution (10 wt%) was prepared using hexane as a solvent. This solution was also spin-coated on the multilayer of PMMA microsphere at 2500 rpm for 1 minute.

2.2 Electron irradiation Experiment

PMMA/silicone grease composite film with its substrate was put into vacuum chamber and irradiated with an electron beam generated from a thermionic electron gun. The irradiating process was carried out at ambient temperature in a vacuum chamber under a pressure of less than 2 x 10-5 torr. The energy of the electron beam irradiating the samples was fixed at 50 keV and the current density of electron beam was changed from 3 to 12 $\mu A/cm^2$ and the total electron fluence was varied from 2.9 x 10^{18} cm^{-2}. Cooling system was used in order to removing a heat produced during the electron irradiation from the sample.

2.3 Morphology study

The pristine films composed of PMMA and silicone grease were initially white but it changed to dark-brown film after the electron irradiation. Figure 1 shows typical FESEM images of the film at each experimental step. At the first step, pristine sample was a multilayer film composed of PMMA microspheres whose diameter is 20 μm (Figure 1a). After silicone grease coating, PMMA microspheres were connected with each other by viscous polydimethylsilioxane (PDMS), which is main component of silicone grease (~ 70 wt%), and some silica nanoparticles (~ 10 wt%) were seen on the PMMA microspheres (Figure 1b). After the electron irradiation, porous hierarchical structure consisted of microparticles connected each other and nanoparticles decorating microparticles (Figure 1c,d). PMMA microspheres became smaller and PDMS became solid bridges connecting microparticles. In addition, silica nanoparticles located on the microparticles and bridges. As a result, highly porous hierarchical structures whose wall was constructed with the combination of micro- and nanoparticles.

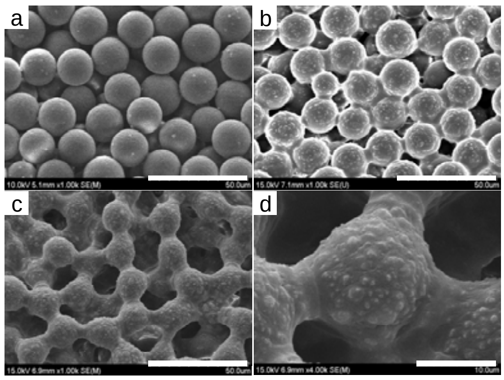

Fig. 1. FESEM images of (a) multilayer of PMMA microspheres, (b) PMMA multilayer with silicone grease coating, and (c) porous hierarchical structure formed after electron irradiation on the film. (d) Magnified image of the wall of hierarchical structure in (c).

2.4 Wettability study

The water contact angle (CA) of pristine inorganic/organic composite film was initially about 110^o (Figure 2a), but dropped water permeated into the film resulting in gradual decrease of CA. After electron irradiation, the film showed the CA of ~ 54^o which means that the irradiated film is hydrophilic (Figure 2b). For the applications to superhydrophobic surface, chemical treatment with (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (Alfa Aesar) was carried out on the surfaces with hierarchical structures. After the surface treatmen, the CA of the surface increased dramatically from 54^o to 169^o which means that the film has superhydrophobic property (Figure 2c). Uniformity of superhydrophobic property was good over silicon wafer with the diameter of 4 inch (Figure 3).

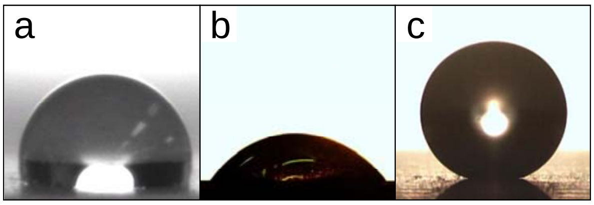

Fig. 2. Water contact angles of the Surface: (a) before electron irradiation, (b) after electron irradiation film, and (c) after surface treatment.

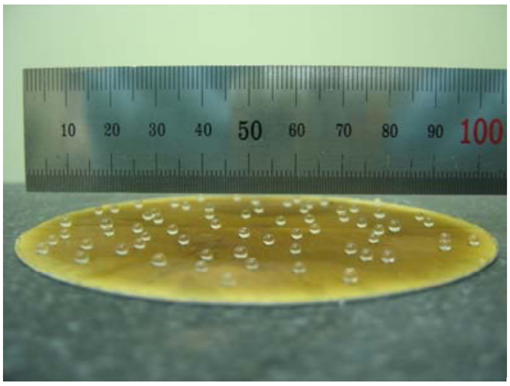

Fig. 3. Superhydrophobic surface fabricated on silicon wafer with the diameter of 4 inch.

3. Conclusions

We have presented the facile route to produce large-area superhydrophobic surface using hierarchical structures fabricated by electron irradiation. This route, using electron irradiation, is one-step process in which no complicated processes are required. Furthermore, large-area fabrication was easily achieved by simply increasing electron irradiation area. In addition, materials used in this experiment are wide-used polymers that are easy to purchase and cheap so that economically competitive. Easy fabrication of large-area superhydrophobic surfaces leads to a real application to various industrial fields.

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