

Letters to the Editor

Title:

Superhydrophilicity on nano-rough carbon surfaces achieved by hyperthermal oxygen-atom beam exposure

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Abstract

In order to investigate a method to increase hydrophilicity on nano-rough carbon surfaces, a nano-rough surface of C₆₀ film and an atomically flat surface of highly oriented pyrolytic graphite (HOPG) were oxidized by hyperthermal oxygen-atom beam exposure and the hydrophilicities of the surfaces were investigated. Superhydrophilicity were achieved on these exposed carbon surfaces, which had low O/C ratio of approximately 28 % and surface roughness (Ra) of approximately 3 nm. The direct oxidations on sp² bonded carbon atoms (basal plane) of these two carbon materials by the exposure of hyperthermal O-atom beam would contribute the superhydrophilicity.

There has been significant interest in the materials science of wetting [1]. Many industrial applications of carbon materials require good surface wetting, including fuel cells [2] and supercapacitors [3]. As the Wenzel theory suggests, the usual method to increase hydrophilicity on hydrophilic surfaces is to make surfaces rough. Especially superhydrophilicity usually demonstrate micro-rough surfaces [4,5]. However, nano-rough surface of TiO₂ demonstrate superhydrophilicity due to photo-induced chemical effect [6,7]. To the best of our knowledge, as far carbon based materials, there is only one study to demonstrate superhydrophilicity on nano-rough carbon surface [8]. The superhydrophilic nano-rough carbon surface is achieved by the aryl-sulfonation treatment. Since the grafted sulfonic acid groups by the treatment are strongly acidic, the functionalized surface has highly hydrophilicity. In addition, this treatment is reported to functionalize graphene basal plane. Although these two effects may greatly improve hydrophilicity on nano-rough carbon surfaces, it is not identified which effects give the great influence to the superhydrophilicity. Previously the basal plane of highly oriented pyrolytic graphite (HOPG) surface was exposed to a hyperthermal oxygen-atom beam and the direct oxidation on defect-free graphite basal planes was observed [9]. It is possible that the effect of basal plane oxidation to improve hydrophilicity on nano-rough carbon surfaces is investigated by hyperthermal O-atom beam exposure.

In this study, a nano-rough surface of C₆₀ film and an atomically flat surface of HOPG, which are composed of sp² bonded carbon atoms (such graphene plane), were used as model of

carbon surfaces and oxidized by exposure of hyperthermal O-atom beam generated from a modified laser plasma-type hyperthermal atom beam facility [10]. The characterization of the oxidized HOPG surface by hyperthermal O-atom beam exposure was previously carried out [8], thus, in this study the surfaces of the C₆₀ films before and after the O-atom exposures were characterized by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Wettabilities of the oxidized carbon surfaces were investigated by measurements of water contact angles.

A C₆₀ film was deposited on silicon wafers with native oxide film by evaporating powdered C₆₀ using a vacuum evaporator. The film thickness was approximately 1 μm measured by scanning electron microscopy (SEM). HOPG surface were freshly cleaved in air. We described previously the details of the modified laser breakdown-type hyperthermal atom beam generator used in this study [10]. Mean translational energy of the hyperthermal O-atom beam was approximately 4.5 eV as measured by the time of flight equipment. The C₆₀ film was located at 30 cm away from the nozzle throat and the flux of the hyperthermal O-atom beam at the position was estimated to be approximately 5×10^{14} atoms/cm²/shot by an etching depth of polyimide. The contact angles were taken at four different points of each sample within a second after dropping the water droplets.

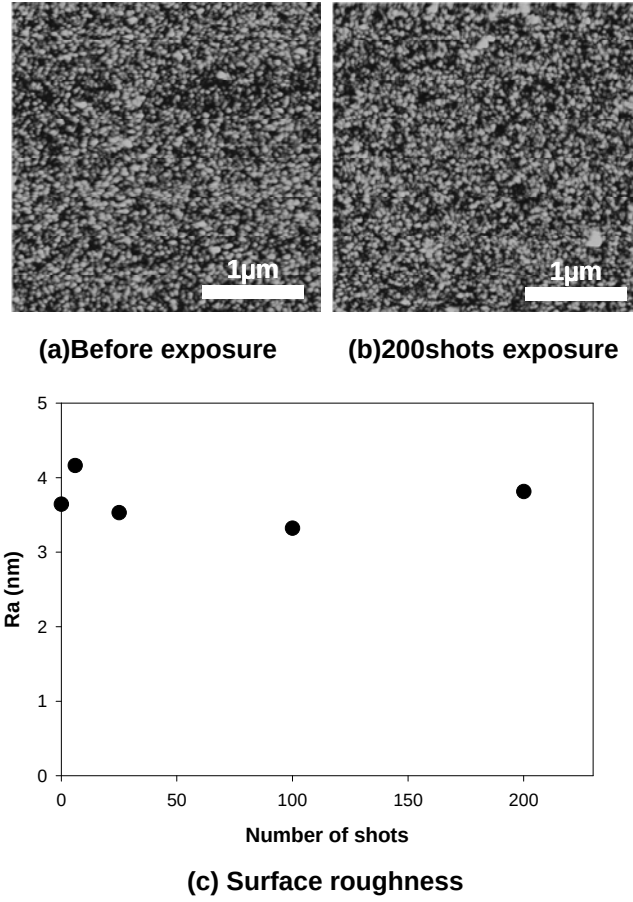
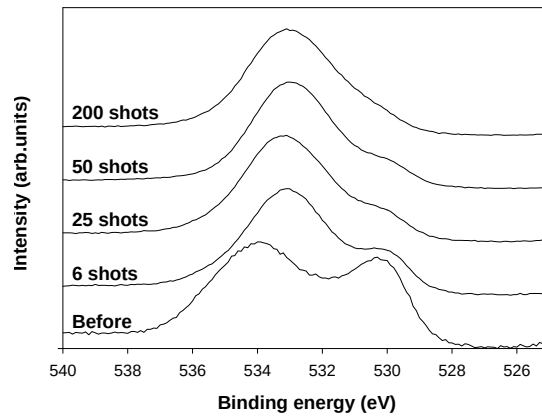
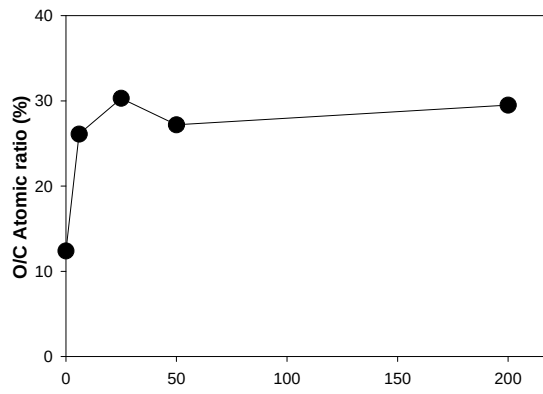


Fig. 1. AFM images of C₆₀ films (a) before and (b) after 200 shots of O-atom beam exposure. (c) Surface roughness (Ra) calculated from AFM images as a function of number of shots.

Figs. 1 (a) and (b) show AFM images of C₆₀ films before and after a 200 shots exposure. Scan size of the AFM images were 3 μm x 3 μm. The protrusions with diameters of approximately 60 nm and heights of approximately 3 nm are observed. C₆₀ were deposited on the Si wafer in the form of clusters. The AFM image of the C₆₀ film with the 200 shots O-atom beam exposure has no notable difference from that before exposure. Fig. 1 (c) shows surface roughness (Ra) as a function of O-atom beam shots. The roughness is not affected by the O-atom shots. Thus the O-atom exposure did not change the nanomorphology of the C₆₀ film.



(a) O1s



(b) O/C ratio

Fig. 2. XPS results of the oxidized C₆₀ films. (a) XPS O1s spectra. (b) Atomic O/C atomic ratio of C₆₀ films as a function of number of shots.

Fig.2(a) shows XPS O1s spectra of the C₆₀ films before and after the O-atom beam exposures. These spectra were normalized. An XPS spectrum of the C₆₀ film before the exposure had two obvious peaks at around 530 eV and 534 eV, which were derived from physically adsorbed oxygen/carbonates [11] and water [12,13], respectively. The O-atom beam exposures caused notable changes of the XPS O1s spectra. After the hyperthermal O-atom beam exposure, the XPS O1s spectra had a peak at around 533 eV derived by C-O and C=O bonds [14], and the peak at around 530 eV decreased, and that at around 534 eV disappeared. Fig. 2 (b) shows O/C atomic ratios of the C₆₀ films calculated from the peak areas of C1s and O1s in XPS spectra. The ratios increased rapidly after the hyperthermal O-beam exposure and reached the saturated value of about 28%. It is concluded that the hyperthermal O-atom beam exposure decreased contaminations such as adsorbed oxygen and water and increased chemical bonds of C-O and C=O. Since C₆₀ is composed entirely of

sp^2 bonded carbon atoms in the form of sphere, there is no prism face in the C_{60} film. Incident hyperthermal O-atom beam on the C_{60} film would collide and oxidize sp^2 bonded carbon atoms.

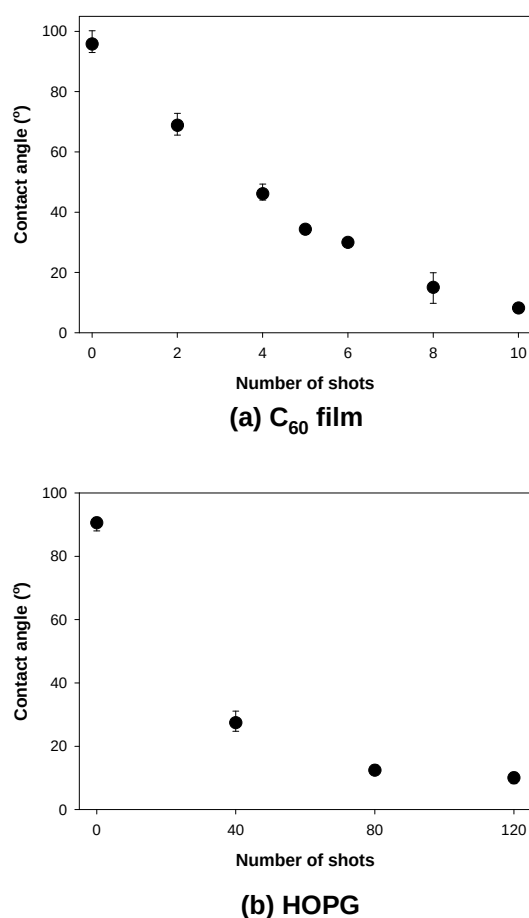


Fig. 3. Relationships between of contact angles of the C_{60} film and HOPG surfaces to the number of hyperthermal O-atom beam shots.

Fig. 3 shows relationships between contact angles of the C_{60} films (a) and HOPG (b) to the number of shots. The contact angle of the non-exposed C_{60} film was 96° and that of non-exposed HOPG surface was 91° . Contact angles of the two samples before the exposures were almost the same. The contact angle of the C_{60} film after the hyperthermal O-beam exposure decreased rapidly, and that after 15 shots was below 5° (spreading wetting), signifying superhydrophilicity. It is interesting to note that even low O-atom fluence achieved the superhydrophilicity for the C_{60} film. Contact angle of the HOPG surface decreased with increasing number of shots. Contact angle of the HOPG surface became below 5° after 160 shots. The decrease rate of the contact angle of the HOPG surface as a function of the number of shots was much lower than that of the C_{60} film. This might

arise from the lower reactivity of HOPG surface with the hyperthermal O-atom beam than the C₆₀ film. The O/C ratios of the superhydrophilic C₆₀ film (15 shots; the estimated fluence is approximately 7.5×10^{15} atoms/cm²) were approximately 28 %. The superhydrophilic HOPG surface (160 shots; the estimated fluence is approximately 8×10^{16} atoms/cm²) had the O/C ratios of approximately 28 % and surface roughness (Ra) of approximately 3 nm [9]. Although these two nano-rough surfaces had different structures (the C₆₀ film has surface where spheres gather together and HOPG has layered structure), these superhydrophilic C₆₀ film and HOPG surface had almost the same O/C ratios of approximately 28 % and surface roughness of approximately 3 nm.

When a flat graphite surface is fully covered (one monolayer) with adsorbed oxygen, O/C ratio of the surface is estimated to be approximately 55 % [9]. This value is almost two times higher than that of the superhydrophilic HOPG surface. Namely, the superhydrophilic HOPG surface had a fifty-fifty mosaic surface of adsorbed oxygen and oxygen-free regions. Since the O/C ratio of the superhydrophilic C₆₀ film had almost the same value as the superhydrophilic HOPG surface, it is considered that the superhydrophilic C₆₀ film also had mosaic surface. In the Cassie/Baxter theory [1], it is assumed that the solid surface is microscopically composed of two different components which have contact angles of θ_1 and θ_2 . The surface area fraction of f_1 and f_2 ($f_1 + f_2 = 1$), and then the contact angle, θ_R , of the liquid on the microscopically mosaic surface can be expressed as

$$\cos \theta_R = f_1 \cos \theta_1 + f_2 \cos \theta_2. \quad (1)$$

Non-exposed C₆₀ film and HOPG surfaces (before exposure) had the contact angles of approximately 90°. Supposing that the fifty-fifty mosaic surfaces are flat and the adsorbed oxygen region has contact angle of 0°, the contact angles on the mosaic surfaces would be approximately 45°. Therefore the O/C ratio of 28 % would not cause the superhydrophilicity on the nano-rough surfaces. In addition, the surface roughness (Ra) of 3 nm is thought to be much too low to achieve the superhydrophilicity. As mention earlier, the aryl-sulfonation treatment, which achieves the contact angle of 5° on the nano-rough carbon surface, is reported functionalize graphite basal plane [7]. A characteristic feature both the aryl-sulfonation treatment and hyperthermal exposure would be

to react with sp^2 bonded carbon atoms (basal plane). Although the detailed mechanism is unknown, oxidations of sp^2 bonded carbon atoms may contribute the superhydrophilicity.

In summary, the superhydrophilicity on the C_{60} film and HOPG were achieved by exposing hyperthermal O-atom beam with the low fluence. The superhydrophilic C_{60} film and HOPG surfaces had surface roughness (Ra) of approximately 3 nm and O/C ratio of approximately 28 %. These factors cannot explain the superhydrophilicity. It is thought that the oxidations of sp^2 bonded carbon atoms due to the hyperthermal O-atom beam exposure may play an important role in the superhydrophilicity.

Acknowledgments

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