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Hydrophobicity and non-thrombogenicity of nanoscale dual rough surface coated with fluorine-incorporated diamond-like carbon films: Biomimetic surface for blood-contacting medical devices

Terumitsu Hasebe [a,b,*], So Nagashima [c], Aki Kamijo [d], Myoung-Woon Moon [c], Yousuke Kashiwagi [a], Atsushi Hotta [a], Kwang-Ryeol Lee [c], Koki Takahashi [e], Takuji Yamagami [f], Tetsuya Suzuki [a]

[a] Center for Science of Environment, Resources and Energy, Graduate School of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa 223-8522, Japan
[b] Department of Radiology, Tokai University Hachioji Hospital, Tokai University School of Medicine, 1838 Ishikawacho, Hachioji-shi, Tokyo 192-0032, Japan
[c] Institute for Multidisciplinary Convergence of Matter, Korea Institute of Science and Technology, Hwarang-no 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea
[d] Department of Transfusion Medicine, Yokohama City University Hospital, 3-9 Hukuura, Kanazawa-ku, Yokohama, Kanagawa 236-0004, Japan
[e] Department of Transfusion Medicine, The University of Tokyo Hospital, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8655, Japan
[f] Department of Radiology, Graduate School of Medical Science, Kyoto Prefectural University of Medicine, Kyoto 602-8566, Japan

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ABSTRACT

We investigated the hydrophobicity and non-thrombogenicity of a nanoscale dual rough surface coated with hydrophobic and non-thrombogenic fluorine-incorporated diamond-like carbon (F-DLC) films. We prepared Si (1 0 0) and a dual rough surface composed of coarse posts and nano-sized fine posts as substrates. DLC film was deposited on the Si substrate, and F-DLC film was deposited on Si or the dual rough surface using radio frequency plasma enhanced chemical vapor deposition method. The surface hydrophobicity of each sample was examined with water contact angle measurements and the non-thrombogenicity was evaluated through incubation with platelet-rich plasma isolated from human whole blood.

The water repellency was dramatically improved on the F-DLC-coated dual rough surface compared with that on DLC-coated Si or F-DLC-coated Si, which had a water contact angle of 130.6°. There was no significant difference in the values for the platelet-covered area between DLC-coated Si and the F-DLC-coated dual rough surface. As DLC is being considered for widespread clinical use as a surface coating for medical devices owing to its non-thrombogenicity compared with other biomaterials, the F-DLC-coated dual rough surface presented in this study still has the potential for clinical use, such as temporary blood-contacting medical devices, to take advantage of its high hydrophobicity.

1. Introduction

Medical implants have been growing in importance, and they are widely used in a variety of clinical fields (such as cardiovascular and orthopedic medicine, as well as dentistry) as key applications for the treatment of diseases and the restoration of missing and defective organ functions. Almost all implants come into contact with blood in the human body; however, the insufficient hemocompatibility of implant surfaces still remains a major problem that causes life-threatening device failure. In order to reduce the risk, the hemocompatibility of biomaterials must be improved.

The inhibition of surface-induced thrombosis is one of the most important issues for blood-contacting medical devices because thrombus formation causes critical device failure with chronic inflammation around implanted sites. Thrombus formation is a complex reaction involving plasma proteins and blood cells. Platelets are anucleate blood particles that play a crucial role in hemostasis and wound healing through adhesion to damaged vascular walls. On the other hand, adhesive capacity is a fundamental factor in clot formation on artificial surfaces after implantation. Therefore, the prevention of platelet adhesion to material surfaces is directly related to the improvement of surface hemocompatibility.

Platelet adhesion to materials depends largely on surface characteristics. Water repellency has been considered to be a characteristic that has a significant effect on platelet adhesion and activation. Many researchers have reported that hydrophobic surfaces tend to inhibit platelet adhesion, which is also the case with highly hydrophilic surfaces [1–10]. As a primary mechanism of thrombus formation on artificial surfaces, it is well known that surface-adsorbed plasma proteins mediate platelet adhesion. Although highly hydrophobic surfaces initially promote the adsorption of large amounts of proteins due to hydrophobic interaction, they might nevertheless become easily desorbed because of its low surface energy [11–13].

* Corresponding author at: Department of Radiology, Tokai University Hachioji Hospital, Tokai University School of Medicine, 1838 Ishikawa-machi, Hachioji, Tokyo 192-0032, Japan. Tel.: +81 42 639 1111.
E-mail address: hasebe@hachioji-hosp.tokai.ac.jp (T. Hasebe).

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On a surface that is flat and chemically uniform, water wettability is fixed univocally as a result of the chemical nature of the solid surface [14]. In order to control surface hydrophobicity, fluorocarbon coatings are usually applied, and it has been reported that surface water repellency reaches approximately 120° of the water contact angle with the use of such coatings [13,15–21]. Here we note that surface water repellency could improve up to nearly 180° of the contact angle in so-called "superhydrophobic states" with the combination of surface geometrical modification and hydrophobic coatings [14]. In general, superhydrophobic surfaces support water drops on the tips of microscopic hydrophobic protrusions with the aid of air trapped in rough surface features [22]. Recently, superhydrophobic materials have been gaining attention as anti-biofouling surfaces for marine devices and biomaterials [23–26]. This is due to particular advantages of those materials, such as surface self-cleaning as a result of high fluid slip and contact area minimization between surfaces and fluids containing bacteria, cells, and proteins in trapped air [27]. Based on these properties, it is assumed that geometrically modified highly water repellent surfaces act to maintain anti-adhesion and anti-adsorption surface properties for blood cells and plasma proteins in blood environment.

In this study, we evaluated the hemocompatibility of a geometrically modified highly water repellent surface. We fabricated a lotus-leaf-like dual-rough surface [28] coated with fluorine-incorporated diamond-like carbon (F-DLC) film, which is hydrophobic and non-thrombogenic [8]. We then investigated the surface wettability and non-thrombogenicity through incubation with platelet-rich plasma (PRP) isolated from human whole blood to explore the possibility of the application of the lotus-leaf-like dual rough surface to blood-contacting medical devices.

2. Materials and methods

2.1. Sample preparation

We prepared Si (1 0 0) and a dual rough surface composed of coarse posts and nano-sized fine posts [28] as substrates. DLC films were deposited on Si and F-DLC films on Si and the dual rough surface using the radio frequency (RF) plasma enhanced chemical vapor deposition (PECVD) method. The RF (13.56 MHz) power and total pressure were fixed at 200 W and 13.3 Pa, respectively. DLC films were deposited from C_2H_2 and F-DLC films from a mixture of C_2H_2 and C_2F_6. The partial pressure of C_2F_6 was fixed at 60% as described previously [8]. The thickness of DLC and F-DLC films was about 50 nm each. In this paper, DLC-coated Si, F-DLC-coated Si, and the F-DLC-coated dual rough surface are denoted as "DLC on flat," "F-DLC on flat," and "F-DLC on dual" as abbreviations, respectively.

2.2. X-ray photoelectron spectroscopy (XPS) analysis

For the manipulation of a dual rough surface, metals are used as masks during the plasma etching process, and they should remain covered with biocompatible materials for clinical use. In this study, Ni (nickel), which is an allergy-causing substance, was used for the mask during the plasma etching process, and F-DLC film [8,9,29,30] was deposited on the dual rough surface. Nearly all metals used as masks were toxic [28]. Thus, the chemical compositions and bonding states of the surface of F-DLC on dual rough surface were measured by XPS (JPS-9000MX, JEOL Ltd., Tokyo Japan) to investigate whether biocompatible F-DLC film completely covered Ni.

2.3. Contact angle measurement

The wettability of "DLC on flat," "F-DLC on flat," and "F-DLC on dual" was evaluated by measuring the static contact angles between a droplet (5 μl) of distilled water and each sample surface. Contact angle measurements were conducted using the sessile drop method with DM 500 (Kyowa Interface Science Co., Ltd.). The results of the experiments are expressed as mean ± standard deviation. Values were compared using an unpaired *t*-test, and differences were considered statistically significant when p was less than 0.05.

2.4. Platelet adhesion and activation

Human whole blood (35 ml) was collected from healthy volunteers and mixed with 5 ml of acid-citrate-dextrose (ACD). The blood was centrifuged at 180 ×*g* for 10 min to separate the blood corpuscles and to obtain platelet-rich plasma (PRP). Subsequently, the rest of the blood was centrifuged at 2000 ×*g* for 20 min to obtain platelet-poor plasma (PPP). The platelet destiny in PRP was adjusted to 3.0×10^5/μl by dilution with PPP. Sample disks (surface area: 10×10 mm^2; $n = 3$ disks for each sample) were washed with phosphate-buffered saline (PBS; pH 7.4) and were then incubated in 24-well plates containing 1 ml of adjusted PRP at 37 °C for 30 min in an atmosphere containing 5% CO_2 gas. Thereafter, the supernatant was discarded and the samples were washed with PBS. Adherent platelets were then fixed for 60 min at room temperature in 1 ml of freshly prepared 1.0% glutalaldehyde. After fixation, the samples were washed and dehydrated in a graded ethanol series (20%, 40%, 60%, 80%, 100% and 100% for 15 min each) as described previously [31]. Dehydrated materials were placed in a vacuum chamber and dried overnight. The completely dried materials were examined by fluorescence microscopy (Eclipse 50*i*, Nikon, Tokyo, Japan). The area covered by platelets per unit area (67,500 μm^2) was investigated via photography using computer-aided image analysis software (Image-Pro-Plus, Media Cybernetics, U.S.A.). Measurements were performed at 10 randomly selected areas for each surface. The results of the experiments are expressed as the means of coverage per unit area ± standard deviation. Values were compared by *t*-test and differences were considered statistically significant when p was less than 0.05. Adhered platelets were then observed using a scanning electron microscope (SEM) (Sirion, FEI, U.S.A.).

2.5. Statistical analysis

The SPSS software version 19 was used for the statistical analysis. The results are expressed as the mean values with the corresponding standard deviation. The platelet-covered area per unit area on each sample was analyzed using one-way ANOVA with post hoc Dunnett's T3 test at a p-value of <0.05.

3. Results and discussion

3.1. XPS analysis

Wide scan spectra in the binding energy range of 0–1000 eV were obtained to identify the elements present on the surface. Fig. 1(a) shows the wide scan spectrum of dual rough surface before the deposition of F-DLC film. The XPS spectrum showed distinct Si2p, Si2s, and Ni2p3/2 peaks, representing both crystalline silicon substrates and metal masks, respectively. Carbon 1s and F 1s peaks shown in Fig. 1(a) indicate the residual fluorocarbon compound formed during the preparation of the dual rough surface with a plasma etching process using CF_4 gas [32]. Fig. 1(b) shows the spectrum of F-DLC coated dual rough surface and no Ni peaks were observed, which indicates that Ni was covered with F-DLC film, suggesting that F-DLC on dual may be a non-allergy-causing material.

3.2. Contact angle measurement

Fig. 2 shows the results of contact angle measurements for "DLC on flat," "F-DLC on flat," and "F-DLC on dual." The water contact angles of "DLC on flat," "F-DLC on flat," and "F-DLC on dual" were 68.8 ± 0.9°, 84.4 ± 1.7°, and 130.6 ± 1.4°, respectively. The contact

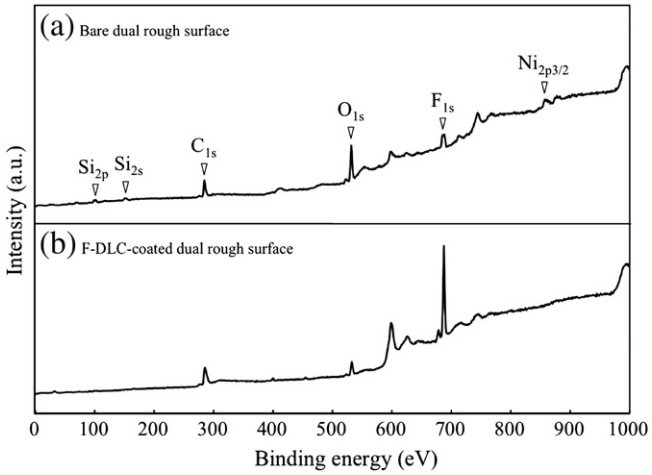

Fig. 1. XPS spectra of dual rough surface (a) before and (b) after deposition of F-DLC film.

angles of F-DLC on flat and F-DLC on dual were significantly higher than that of DLC on flat ($p < 0.05$). As has been described above, surface water repellency could be increased to approximately 120° by chemical modification of the surface. In general, a surface showing a water contact angle of over 150° is defined as superhydrophobic. The water contact angle of the "F-DLC on dual" surface indicated a value between 120° and 150°. There is still no common definition for this water contact angle range. Roach et al. proposed that a roughened surface showing a contact angle between 120° and 150° should be termed "ultrahydrophobic" [33].

The increase in contact angle from 68.8 ± 0.9° ("DLC on flat") to 84.4 ± 1.7° ("F-DLC on flat") was presumably due to the polar bonds such as C–F and C–CF present on the uppermost surface of the F-DLC film, as we reported previously [8].

The increase in contact angle from 84.4 ± 1.7° ("F-DLC on flat") to 130.6 ± 1.4° ("F-DLC on dual") would be attributable to the change in surface morphology. According to the Cassie and Baxter theory [34], the contact angle on a rough surface that has air trapped by posts is higher than that on a flat surface. The dual rough surface used in this study had coarse (height: 352.0 ± 53.2 nm, diameter: 360.5 ± 63.1 nm) and fine (height: 90.1 ± 11.3 nm, diameter: 71.5 ± 10.4 nm) posts [28]. Therefore, "F-DLC on dual" could hold air pockets between the solid phase and the liquid phase, which would result in the increase in hydrophobicity.

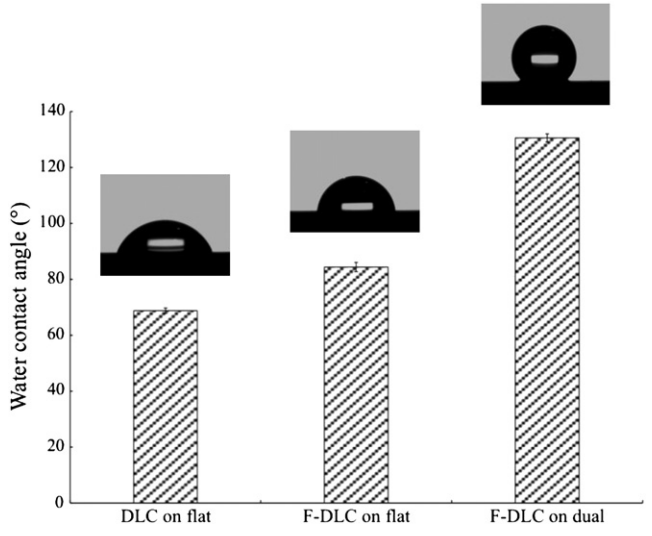

Fig. 2. Contact angle of 5-μl water droplet on each sample. Mean ± SD (n = 5).

3.3. Platelet adhesion and activation

We examined the behavior of adherent platelets on each sample using the glutalaldehyde induced fluorescence technique (GIFT) [31]. GIFT uses the epifluorescence of glutalaldehyde-fixed platelets as detected by fluorescence microscopy and is suitable for opaque and transparent materials.

In this study, using computer-aided image analysis, a platelet-covered area was designated as an index for surface thrombogenicity. Both the number of platelets and the changes in morphological shape of activated platelets contribute to the platelet-covered surface area of the substrate. Thus, calculating the platelet-covered area/unit area results in an index that reflects platelet adhesion and activation.

Fig. 3 shows the representative fluorescence microscopic images of adherent platelets for each sample and Fig. 4 indicates the platelet-covered area per unit area for each sample. The value for "F-DLC on flat" was significantly lower than that for "DLC on flat," and there were no significant differences in the values for "DLC on flat" and "F-DLC on dual." As DLC is being considered for widespread clinical use as a surface coating for medical devices owing to its non-thrombogenicity, "F-DLC on dual" presented in this study has potential for clinical use. However, the results obtained here did not correspond with our expectations that "F-DLC on dual" would dramatically inhibit platelet adhesion and activation, as it exhibited the most pronounced hydrophobic properties of all of the samples.

This was probably due to a decrease in hydrophobicity and an increase in surface area caused by the disappearance of air pockets between the solid phase and the liquid phase. Fig. 5 shows an SEM image of adherent platelets on the surface of "F-DLC on dual." This image demonstrates the proliferation of platelet pseudopodia in the space between the posts. This indicates that air, which had been thought to exist during incubation with PRP, would disappear so that pseudopodia (small legs) of platelets could penetrate the space. Such disappearance of air pockets would induce the following two phenomena: (1) increase in blood-contacting surface area, which would result in an increase in the value for the platelet-covered area on the surface; and (2) transition of the surface from a Cassie state to a Wenzel state, which could account for a decrease in hydrophobicity.

Tuteja et al. have reported that if the equilibrium contact angle (θ) is less than the local geometric angle of the surface texture (ψ), the net traction on the liquid–vapor interface is downward, promoting the imbibition of the liquid into the solid structure, leading to a wetted interface [35]. In our case, ψ and θ are estimated to be over 90° and around 85°, respectively, and therefore, imbibition of the liquid could occur. Although "F-DLC on dual" exhibited enhanced hydrophobicity during the static contact angle measurement, the surface may have been wetted after immersion in PRP. In fact, such a phenomenon has been observed for lotus leaves [36].

Koh et al. investigated the effects of aspect ratio and interspacing, or density, of protruding surface features on fibrinogen and platelet adsorption [37]. They have reported that (i) increasing interspacing of the protrusions (>200 nm) results in the entrapment of platelets and their subsequent activation because of the increase in the effective contact surface area; and (ii) increasing aspect ratio reduces the number of adherent platelets owing to the inability of the platelets to form stable contacts with the reduced surface area for the attachment. When we take a look at the posts on our sample surface, the interspacing among the coarse posts is around 300 nm, while that among the fine posts is less than 100 nm. Based on the findings by Koh et al., we can raise a hypothesis that platelets had a chance to interact with the fine posts existing among the coarse ones, whereas

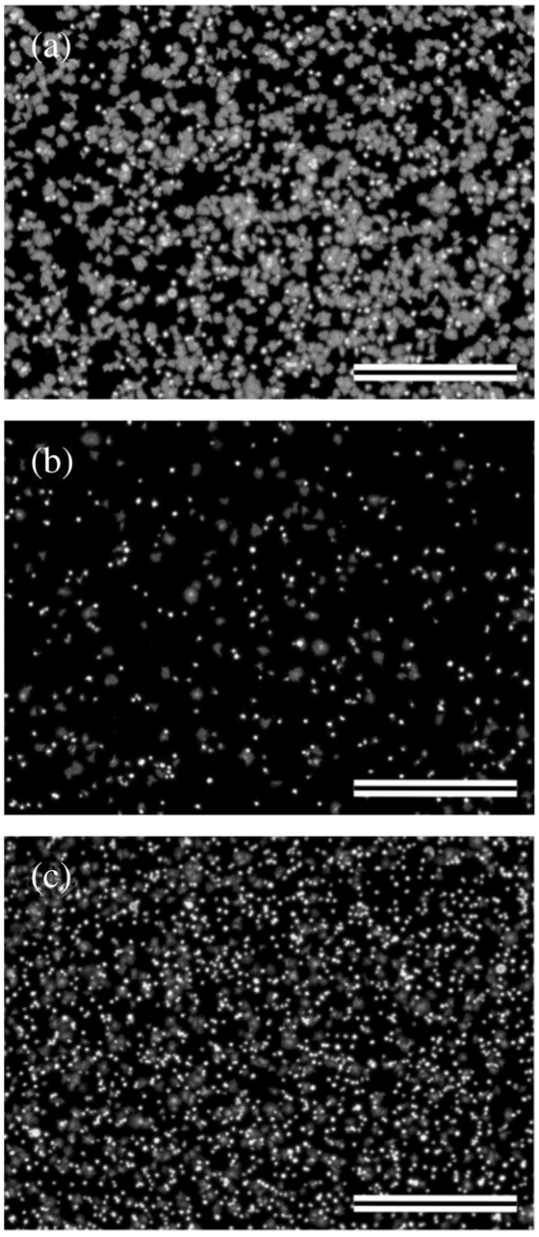

Fig. 3. Representative fluorescence microscopic images of adherent platelets on (a) DLC on flat, (b) F-DLC on flat and (c) F-DLC on dual. Bar indicates 100 μm.

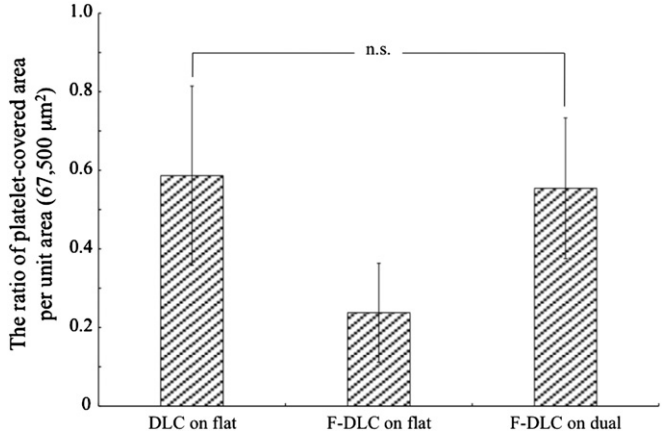

Fig. 4. Ratio of platelet-covered area per unit area (67,500 μm^2) on each sample.

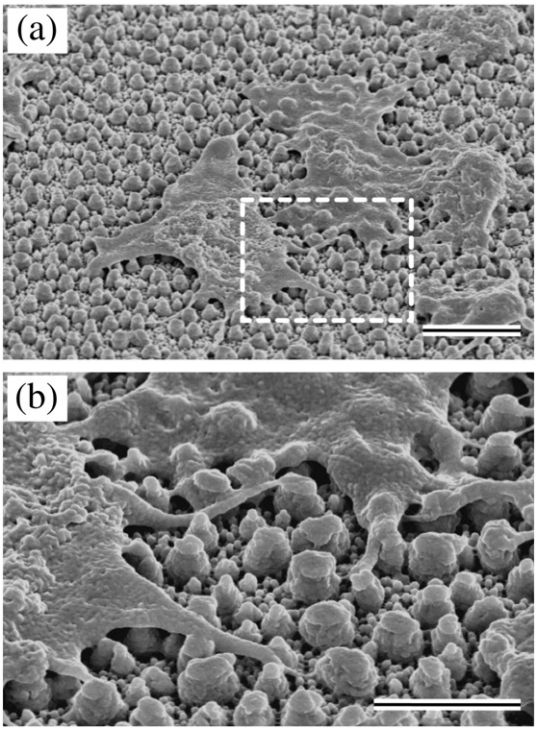

Fig. 5. SEM image of adherent platelets on "F-DLC on dual." (a) The outer shape of adherent platelet on dual rough surface and (b) detail of contact between platelet pseudopodia and micron-nano posts. Bar indicates (a) 1 μm and (b) 2 μm.

those could not contact the very bottom surface among the fine posts, and the SEM images of adherent platelets on the surface of "F-DLC on dual" shown in Fig. 5 can support the hypothesis.

To take advantage of the high surface hydrophobicity of "F-DLC on dual," air pockets should be maintained during the experiment. The incubation time for the samples with PRP was 30 min. This means that our study protocols were intended to reflect application of the engineered surface to implantable devices in blood vessels. Based on these criteria, "F-DLC on dual" may not be suitable for permanent medical implantation in the blood. A dynamic evaluation system (e.g., 1, 5, 10 and 20 min after incubation with PRP) that satisfies the requirements for temporary blood-contacting medical devices should be developed. Further investigations on the effects of interspacing and aspect ratio of the dual posts on the adhesion and activation of platelets are also important for optimizing the surface topography for improved non-thrombogenicity. Continued research is needed to investigate the further potential of medical applications for "F-DLC on dual."

4. Conclusion

We investigated hydrophobicity and non-thrombogenicity of a nanoscale dual rough surface coated with hydrophobic and non-thrombogenic F-DLC film. We prepared three samples: DLC-film-coated Si ("DLC on flat"), F-DLC-film-coated Si ("F-DLC on flat") and an F-DLC-film-coated dual rough surface ("F-DLC on dual"). The dual rough surface was composed of coarse posts and nano-sized fine posts. DLC films and F-DLC films were deposited on Si and the dual rough surface using the radio frequency (RF) plasma enhanced chemical vapor deposition (PECVD) method. The surface hydrophobicity and non-thrombogenicity of each sample were examined based on water contact angle measurements and by calculating the platelet-covered area of each sample surface after incubation with PRP isolated from human whole blood, respectively.

Hydrophobic properties were dramatically improved with "F-DLC on dual" compared with "DLC on flat" and "F-DLC on flat," which had a water contact angle of 130.6°. There was no significant difference

between the value for the platelet-covered area for "DLC on flat" and that for "F-DLC on dual". As DLC is being considered for clinical use as a surface coating for medical devices owing to its non-thrombogenicity compared with other biomaterials, "F-DLC on dual" presented here still has potential for clinical use. However, continued research is needed to investigate the further potential for medical applications of the surface (e.g., temporary blood-contacting medical devices such as surgical knives, catheters, and the like).

Prime novelty statement

In the present study, we focused on the topographically modified water-repellent surface (a "lotus-leaf-like" surface coated with fluorinated DLC (F-DLC)) as antithrombogenic material for medical applications. The antithrombogenicity of topographically modified F-DLC-coated surface with high water-repellency was reported in this paper.

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