A Facile Fabrication of Superhydrophobic Films by Electrophoretic Deposition of Hydrophobic Particles

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We demonstrated a fabrication of superhydrophobic colored films by the electrophoretic deposition (EPD) of hydrophobic pigment particles on substrates. The superhydrophobic films showed various colors such as black, white, blue, and green.

The wettability of solid surfaces, which is estimated by the water contact angle (CA), is an important property in surface chemistry. When solid surfaces show a water CA greater than 150°, such surfaces are called superhydrophobic surfaces. Superhydrophobic surfaces are found in nature (e.g., lotus leaves and legs of water sliders), and the origin of this superhydrophobicity has been investigated.[1] Recently, superhydrophobic films have drawn attention for not only fundamental research but also for practical application due to their self-cleaning ability.[2] It has been proposed that solid surfaces show a superhydrophobicity when they have both rough surfaces and the low surface energy. From this viewpoint, superhydrophobic surfaces have been prepared by enhancing the surface roughness, followed by deposition of low surface energy materials. To roughen the surface structure and reduce their surface energy, various excellent methods have been proposed.[2] In addition, the development of industrial products with a self-cleaning ability is a recent hot-topic, for example, superhydrophobic cloths were fabricated by modification with suitable gold micro/nanostructures.[3] For the surface of these industrial materials, optical properties such as transparency, reflectivity, and color are important. Recently, transparent or highly reflective superhydrophobic films were fabricated,[4,5] but as far as we know superhydrophobic films with various colors have not been obtained. We now report a facile fabrication process for colored superhydrophobic films by the electrophoretic deposition (EPD) of commercially available pigments. The EPD method allows the coating of substrates with a great variety of particles (e.g., metal, metal oxide, ceramics, and polymer), and its simplicity is also important.[6] EPD is a cost-effective method usually requiring simple equipment as well as being easy to scale-up to large dimensions. EPD is achieved via the motion of charged particles, dispersed in a suitable solvent, towards an electrode under an applied electric field. EPD is a simple and inexpensive process; however, the fabrication of superhydrophobic films using EPD has not been achieved. In this study, superhydrophobic colored films are fabricated by EPD of hydrophobic pigment particles, which are commercially available.

We first examined the fabrication of carbon black films using the EPD process. By applying a voltage (30 V), carbon black dispersed in ethanol containing $MgCl_2 \cdot 6H_2O$ that provided a charge to carbon black migrated to the substrates to form films. The water CA measurement of the resulting carbon black film indicated that the carbon black films have superhydrophobicity. It is interesting that such a simple fabrication process (i.e., only the EPD of commercially available particles) produced the superhydrophobic surfaces, because most methods for constructing superhydrophobic surfaces usually require specialized equipment and/or complicated processing (temperature, substrate, and chemicals). Thus, the fabrication of superhydrophobic surfaces by EPD of commercially available particles was investigated in more detail. Carbon black, activated carbon, vapor-grown carbon nanofibers (VGCFs), titanium dioxide (TiO_2), β-type copper phthalocyanine (β-CuPc), and phthalocyanine green ($CuPcBr_xCl_y$) were used as the hydrophobic particles. Carbon black, TiO_2, β-CuPc, and $CuPcBr_xCl_y$ are well-known pigments used in the various fields. Activated carbon is a functional carbonaceous material with a high surface area, and VGCF is a carbonaceous nanomaterial. As for only TiO_2, hydrophobic surface modification was carried out with silane coupling reagents, because the original surface of the TiO_2 particles is hydrophilic due to the presence of hydroxy groups. Other particles did not receive such treatment, because their surfaces have hydrophobicity. The detail experimental procedures including the EPD process is shown in Supporting Information.[8] Figure 1 shows photographs of the carbon black, TiO_2, β-CuPc, and $CuPcBr_xCl_y$ films prepared by the EPD process. It was obvious that all the particles were fixed on the substrate as films which showed various colors such as black, white, blue, and green. Activated carbon and VGCFs also formed black films (not shown in figure). The water CAs of these colored films are as follows; 159° for the carbon black film, 157° for the activated carbon film, 160° for the VGCF film, 159° for the TiO_2 film, 160° for the β-CuPc film, and 160° for the $CuPcBr_xCl_y$ film (the shape of a water droplet on the carbon black film is shown at the inset of Figure 2a), suggesting that all the colored films have superhydrophobicity. In addition, a variety of conductive materials, such as Fe, Cu, and Al plates, could be used as substrates for the fabrication of superhydrophobic films. These results indicate that a variety of particles can become a superhydrophobic film on conductive substrates using the facile EPD process. As for the strength, films could steadily repel the running water without peeling, because particles on substrates would be connected by Mg metals formed when Mg^{2+} ions are reduced on cathode during EPD process. However, films are broken and lose superhydrophobicity by scratching.

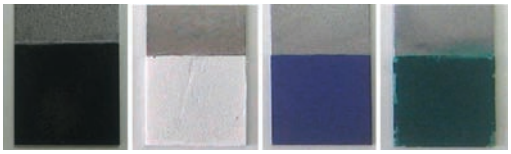

Figure 1. Superhydrophobic colored films. (a) carbon black, (b) TiO_2, (c) β-CuPc, and (d) $CuPcBr_xCl_y$.

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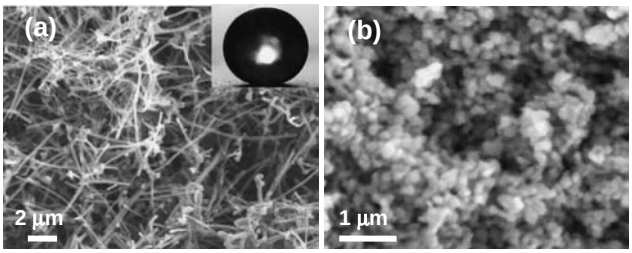

Figure 2. SEM images of surface structure of superhydrophobic (a) VGCF films and (b) TiO_2 films.

The wettability of films was strongly dependent on the EPD conditions. For example, the films which were fabricated for the first time by the EPD did not show superhydrophobicity (water droplets soaked into these films). However, the hydrophobicity of films increased as the EPD was repeated using the same bath. Since Mg^{2+} that provides a charge to hydrophobic particles is consumed through the EPD process, the concentration of Mg^{2+} in the bath may related to the hydrophobicity of the formed films. In fact, the hydrophobicity of the films varied with the concentration of the $MgCl_2 \cdot 6H_2O$ in the bath. However, at this moment, the reason why the hydrophobic properties are affected by the EPD conditions cannot be clearly explained.

Figure 2 shows the surface SEM images of the VGCF and TiO_2 superhydrophobic films. For the VGCF films, many nanofibers of ca. 200 nm diameter were present, and pores of their fibrous structure were observed. In addition, the 3D structure of the VGCF films indicated rough surface structures (Figure S1).[8] For the TiO_2 films, they consisted of particles of submicron diameter, and the rough surface structures are confirmed. It has already been reported that solid surfaces with a low surface energy and a high roughness have high hydrophobicity. The trapping of air components in the rough surface structure causes an increase in the water CA, because air is absolutely hydrophobic material (water CA is 180°). Therefore, air plays an important role for the development of the superhydrophobicity, for example, even if films that consist of hydrophilic materials can show the superhydrophobicity when a large amount of air is trapped in the film surface.[7] The results in Figure 2 strongly suggest that films prepared by the EPD of hydrophobic particles have a rough and porous structure. This would be the reason why the colored films showed superhydrophobicity.

As comparative experiments, films were prepared by pressing the hydrophobic particles on the substrate. All the particles turned into films, but none of the films showed a superhydrophobicity. The water CAs of the films prepared by pressing were as follows: 126° for the VGCF films, no measurement because of high hydrophilicity (water drops immediately soaked into the films) for the activated carbon films, 112° for the TiO_2 films, 127° for the β-CuPc films, and 142° for the $CuPcBr_xCl_y$ films, indicating that the EPD is an essential process for fabricating the superhydrophobic films even if hydrophobic particles are used as constituents of the films. To examine their surface structure in detail, the cross-sectional SEM images of these films were measured. Figure 3 shows cross-sectional SEM images of the VGCF films prepared by EPD (Figure 3a) and by pressing (Figure 3b). The white parts in these SEM images show the presence of cured resin for preparing cross-sectional specimens. Thus, the white parts correspond to the area where air was present. On the other hand, the black parts denote the VGCFs. Obviously, the films prepared by EPD contain a larger amount of air than the films prepared by pressing. Therefore, this must be the reason why the films prepared by EPD shows superhydrophobicity, while the films prepared by pressing did not have a superhydrophobicity. The EPD process would produce porous films according to the following mechanism. The films immediately after being prepared by the EPD must contain ethanol, and this is removed by drying at room temperature. During this drying process, ethanol would be replaced with air, leading to the formation of films with a large amount of air.

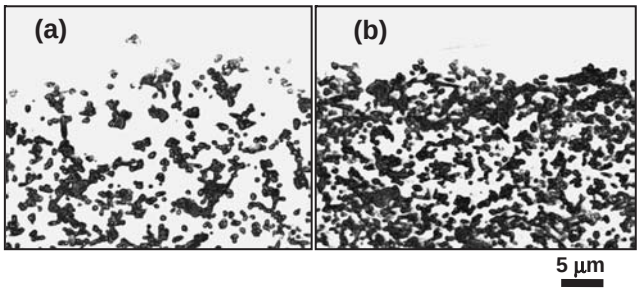

Figure 3. Cross-sectional SEM images of VGCF films. (a) EPD process, and (b) press process.

In conclusion, the superhydrophobic films with colors such as black, white, blue, and green could be easily fabricated by the EPD of hydrophobic particles. Superhydrophobic colored films were formed on a variety of substrates as long as they have an electrical conductivity. Using the EPD process, superhydrophobic films which consisted of various particles could be prepared, and so these films must have not only hydrophobicity but also characteristic properties of each particle. In this way, our fabrication process of superhydrophobic films can be expected to be use in water-resistant coatings in various fields.

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References and Notes

1 a) L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, *Adv. Mater.* **2002**, *14*, 1857. b) C. W. Extrand, *Langmuir* **2003**, *19*, 3793. c) M. Nosonovsky, B. Bhushan, *Langmuir* **2008**, *24*, 1525.
2 a) X. Feng, L. Jiang, *Adv. Mater.* **2006**, *18*, 3063. b) M. E. Abdelsalam, P. N. Bartlett, T. Kelf, J. Baumberg, *Langmuir* **2005**, *21*, 1753. c) H. Li, X. Wang, Y. Song, Y. Liu, Q. Li, L. Jiang, D. Zhu, *Angew. Chem., Int. Ed.* **2001**, *40*, 1743. d) N. K. Shrestha, G. Kobayashi, T. Saji, *Chem. Lett.* **2004**, *33*, 984.
3 T. Wang, X. Hu, S. Dong, *Chem. Commun.* **2007**, 1849.
4 a) H. Yabu, M. Shimomura, *Chem. Mater.* **2005**, *17*, 5231. b) J. Bravo, L. Zhai, Z. Wu, R. E. Cohen, M. F. Rubner, *Langmuir* **2007**, *23*, 7293.
5 L. Shen, J. Ji, J. Shen, *Langmuir* **2008**, *24*, 9962.
6 P. Sarkar, P. S. Nicholson, *J. Am. Ceram. Soc.* **1996**, *79*, 1987.
7 E. Hosono, S. Fujihara, I. Honma, H. Zhou, *J. Am. Chem. Soc.* **2005**, *127*, 13458.
8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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