



Article Fingerprint Blurring on a Hierarchical Nanoporous Layer Glass

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Abstract: A fingerprint blurring phenomenon on a hierarchical nanoporous layer (HNL) glass has been discovered and experimentally investigated. The HNL glass was prepared by a simple one-pot etching as reported by the authors. IR absorption spectra and water contact angle revealed that the blurring does not come from a chemical decomposition but a transportation of the fingerprint components, and the capillary action drives the transportation, not the thermal diffusion. The fine pores in the HNL was indicated to develop the strong capillary force to blur the fingerprint. The fingerprint blurring phenomenon on the HNL can be a candidate for the third anti-fingerprint methodology after the popular ones of low frictional surfaces and anti-glare surfaces.

Keywords: anti-fingerprint; nanoporous; glass; capillary action

1. Introduction

Silicate glasses have been widely used in various products for thousands of years. Some good examples include window glass, dishes, bottles, lens, and display panels. The popularity of glass mainly comes from its high optical transparency and its mechanical strength suitable for practical use. Therefore, fouling is a major issue against the practical use of glass materials because it scatters or absorbs light to lose its transparency. Fouling comes from rain, dust, food, and users' fingerprints, for example.

Fingerprints are known to be challenging to remove from various surfaces and unavoidable where humans directly handle the product. The only organ on the fingertip skin is an eccrine sweat gland, which forms an aligned pattern of its uplifted opening section. The secretion from the gland consists mainly of water (ca. 98%), organics like amino acids and proteins, and inorganics like salts [1,2]. Practically, however, there are many materials on the fingertip, because hands generally touch various things in daily life, such as sebum secreted at other parts of the body and other exogenous substances. When the fingertip touches something, the materials on it move onto the touched surface to form a pattered mark which we call fingerprint [3]. According to the situation described above, the composition of the attached fingerprint widely varies. This makes the fingerprint removal technology complicated and challenging to reach versatility [4–6].

There are two significant methodologies to give a surface anti-fingerprint properties. A popular one is a fluorine coating that suppresses the amount of fingerprint adhesion by making the surface low friction [7,8] This type of surface has an issue of losing its low frictional property over time, though it is used widely in various products. The other one is an anti-glare surface on which a micro-texture is molded to make fingerprint unclear [9]. Though this type has better stability in comparison with the former, the texture also scatters light to reduce transparency.

In addition to the two methodologies, there could be another one that makes a fingerprint diffuse or obscure. A fingerprint, however, is so strongly adhesive that there no material has been able to create adequate diffusion. Though there were some attempts using oleophilic surfaces to blur the fingerprint, they worked only for a small amount of attachment.

We have realized a new antifouling material with a hierarchically nanoporous layer (HNL) on a silicate glass in recent years [10,11]. The HNL has a three-dimensionally continuous porous structure like a sponge, with its porous size decreasing from the apparent surface toward the buried region. This topological specification results in an anti-reflective property for a wide range of optical waves based on the moth-eye effect. Furthermore, an overwhelmingly sizeable, intrinsic surface area, compared to the apparent surface, geometrically extends the surface-free energy, which gives the HNL robust and long-lived superhydrophilicity. The superhydrophilic surface is generally known to exhibit antifouling and antifogging properties [12], and the HNL reportedly does, too. Another practically unique point of the HNL is ease of its structure formation. The complicated structure arose from a simple one-pot etching. Another point is that the layer is formed not by any deposition but by etching, which keeps itself firmly on the bulk material due to the intrinsic connectivity.

Recently, we have found that there is a blurring phenomenon of a fingerprint attached to the HNL glass, which could be a candidate for the third anti-fingerprint material described above. In this work, we characterized the fingerprint blurring on the HNL and discussed the transport direction of the fingerprint components.

2. Materials and Methods

The HNL glass samples were prepared by following the method described in our previous work [10]. We used a soda-lime glass (Matsunami Glass) as a base material. The pristine glass pieces were heated at 120 °C for 22 h in a sodium-bicarbonate aqueous solution of 0.5 mol dm⁻³ to form the HNL on their surfaces. The samples were finally rinsed in deionized water then dried before the tests and investigations. The obtained HNL structure was confirmed by a field-emission scanning electron microscope (Hitachi High-Technologies, SU-8230, Tokyo, Japan).

We applied a fingerprint attachment condition that is commonly used for researches on fingerprint: sebaceous condition [13]. In the sebaceous condition, a donor firmly touched samples after washing their hands carefully with soap and then rubbing their forehead. The donor in this work was a Japanese woman aged in her twenties.

In addition to the optical observation of the attached fingerprints from the viewpoint of their temporal change, we also performed the infrared (IR) absorption spectroscopy using an FT-IR (Perkin-Elmer, spectrum-one, Waltham, U.S.A.) under a transmit setup in a dried nitrogen atmosphere. The IR measurements were conducted in different parts to define the material transportation during the blurring phenomenon: the central part of the attached fingerprint and a blurred region outside the initial fingerprint.

3. Results and Discussion

The HNL we used here had a thickness of $0.5 \,\mu\text{m}$ and pore size of $20\text{--}30 \,\text{nm}$ at the apparent surface as shown in Figure 1. The sample surface exhibited strong superhydrophilicity with a water contact angle of less than 5°. [10] Low optical reflectivity of c.a. 0.5% across the visible wavelength was also typical with the HNL glass as shown in Figure 1c.

Figure 2 shows the optical micrographs of a fingerprint on HNL glass and untreated glass. As shown in the figure, the fingerprint on the HNL blurred within 10 min to partially disappeared in contrast to the untreated glass where the fingerprint remained unchanged. Even on the non-porous material surface, the ridge may be blurred due to the deterioration of the fingerprint within a few days after adhering [14–16], but on the HNL glass, the ridge was smeared in an overwhelmingly short time. This phenomenon could come from chemical decomposition or some transportation of the fingerprint components.



Figure 1. The HNL characterization. (**a**) Cross-sectional view and (**b**) surface view of the HNL in SEM micrography. Both micrographs were obtained without any metal deposition. (**c**) Single-side reflectivity spectrum of HNL and untreated glass.



Figure 2. Optical micrograph of fingerprint on (**a**,**b**) HNL and (**c**,**d**) untreated glass taken (**a**,**c**) just after the fingerprint attachment and (**b**,**d**) 10 min later. The fingerprint only on HNL blurred as shown in (**b**) though that on the untreated glass remained unchanged.

We performed FT-IR measurement to define the quantitative change of the attached chemical components. Figure 3 shows the IR absorption spectra measured at the central part of HNL glass before and after the fingerprint attachment. As shown in the figure, absorption peaks at 2860 and 2930 cm⁻¹ corresponding to a fatty acid alkyl group [17,18] appeared by the fingerprint attachment.

The alkyl-originated absorption just after the fingerprint attachment and 10 min later were compared in the figure. What is to be noted here is that the absorption peaks remained unchanged during the fingerprint blurring that was observed in Figure 2. This means there was neither decomposition [19] nor removal of the organic component in the fingerprint during the blurring. Therefore, the cause of the fingerprint blurring on HNL is indicated to be some transportation of the attached materials.



Figure 3. IR absorption spectrum of HNL before and after the fingerprint attachment. No absorption was detected before the attachment though obvious absorption peaks appeared after the attachment and kept themselves unchanged during the blurring shown in Figure 2.

The fingerprint blurring persisted for a long time to form a large ring around the initial fingerprint after a week (Figure 4a). Figure 4b shows IR absorption spectra measured around the initial fingerprint before and after the spreading. As shown in the figure, the spread material contained the fatty acid alkyl group, which was also in the initial fingerprint (Figure 3). In other words, the fingerprint blurring progresses with the transportation of the fatty acid in the HNL as in chocolate [20].



Figure 4. A long-time change of the fingerprint on HNL. A spreading ring appeared around the fingerprint as shown in (**a**). The IR spectra measured at the ring indicated in (**a**) detected the fatty acid alkyl group detected in Figure 3 as shown in (**b**).

The water contact angle was also measured on and around the attached fingerprint. Because the volume of the water droplet was 2 μ L, its footprint was small enough to differentiate each region.

As shown in Table 1, the fingerprint-attached region exhibited weak hydrophilicity other than the pristine HNL, which is consistent with the IR absorption in Figures 3 and 4.

Sample/Position	Pristine HNL	on Fingerprint	Peripheral Area
Water Contact Angle	7.2°	40.8°	8.0°

Table 1. Water contact angle on fingerprint-attached HNL.

However, the spreading ring around the initial fingerprint had the same superhydrophilicity as the pristine HNL, which appears to be inconsistent with Figure 4, revealing that the spreading ring contained a fatty acid. Since the fatty acid with alkyl chain lowers the hydrophilicity as on the initial fingerprint region, the spread ring region with the acid as indicated in Figure 4 should not have such strong hydrophilicity as on the pristine HNL.

The superhydrophilicity on the spreading ring provides a clue to elucidate the driving force for the fingerprint blurring. The low water contact angle was formed by wetting a large intrinsic surface area from the apparent surface of the samples. This means the inner surface in the vicinity of the apparent surface was clean and not covered by a transported hydrophobic fatty acid. Then, the hydrophobic molecules detected by the IR absorption is supposed to be in a deeper region.

There could be two mechanisms for this transportation of molecules where the gravity is negligible: surface diffusion and capillary action. If the former were dominant, the molecules would spread on the inner surface isotropically. Therefore, surface diffusion is inconsistent with the experimental indication mentioned above.

Since the HNL has a hierarchical structure as shown in the Figure 1, deeper pores have a smaller size that result in stronger capillary action for an affinity liquid. Capillary force is inversely proportional to pore size. Therefore, the existence of the fatty acid only in a deeper region of HNL indicates that its transportation was driven by capillary action [21,22].

4. Conclusions

In this work, we have found that HNL has a new type of anti-fingerprint property, which is fingerprint blurring. The fingerprint attached to HNL spreads and blurs in a time scale of minutes that can never occur on the untreated glass. This phenomenon was revealed to originate from the transportation of fatty acid contained in the fingerprint. Furthermore, the transportation has been indicated driven not by thermal diffusion but by capillary action in fine pores in the buried region of HNL due to its hierarchy.

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