

Facile Fabrication of Superhydrophobic Cellulose Materials by a Nanocoating Approach

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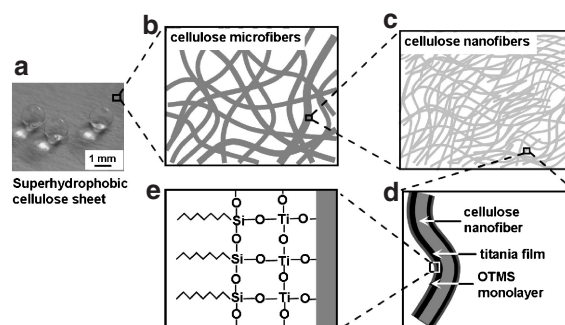
Superhydrophobic cellulosic materials with remarkable self-cleaning ability and satisfactory long-term chemical stability were fabricated by depositing self-assembled silane monolayer onto ultrathin titania film precoated nanofibers of natural cellulosic substances without altering the initial material structures and morphologies.

Self-assembled materials with advanced hydrophobic properties have been attracting increasing interests due to their importance both in fundamental research and practical applications. It is known that superhydrophobicity is generally a result of the micro- to nanoscaled hierarchical surface structure of the material, namely, the desired microscaled structural roughness and the particular thin low surface energy coating layer applied.^{1–4} The inherent physicochemical properties of the pristine materials play determinative role in the practical applications of the man-made superhydrophobic material. Inorganic substrates (e.g., glass slide,⁵ silicon wafer,⁶ and metal plate⁷) are less mechanically flexible, while polymeric substrates (like polyester textiles⁸) lack ideal biodegradability. Cellulose is a biodegradable and renewable natural biopolymer,⁹ and as a result of the environmentally friendly properties and mechanical flexibility of cellulose, transformation of such highly hydrophilic substances into superhydrophobic materials would improve the growth potential of them.

Cellulose substances like filter paper, cotton, and cloth have been endowed with hydrophobic properties via various approaches, such as atom-transfer radical polymerization,¹⁰ polymethylsiloxane coating,¹¹ gold nanoparticle immobilization,¹² and plasma etching.¹³ However, the development of facile, effective, and inexpensive methodology to produce superhydrophobic cellulose materials, in particular without changing the initial unique morphological and structural features of the raw cellulose, is still in strong demand and of great challenge. This is mainly due to the chemical inertness of cellulose, which makes it difficult for surface modification to be effectively achieved. We have succeeded in depositing nanometer-thick metal oxide coating onto nanofiber surface of natural cellulose substances (e.g., filter paper).¹⁴ Such metal oxide (e.g., titania) nanocoating provides a unique and ideal platform for further assembly of various guest substrates onto the cellulose nanofiber surface, resulting in different functional nanoarchitectures.

By taking advantage of the ultrathin titania film coating of natural cellulose substances, here we developed a practical approach to fabricate superhydrophobic cellulose materials by depositing long alkyl chain silane monolayer onto the ultrathin titania film precoated cellulose fiber surface. Commercial filter paper was chosen as the raw material, and the resultant material possessed stable superhydrophobicity.

Flat quartz plate modified with 10-layer titania film (thickness ca. 5 nm) and octyltrimethoxysilane (OTMS) monolayer



Scheme 1. Schematic illustration of the superhydrophobic cellulose materials fabricated by nanocoating with ultrathin titania/OTMS films.

(denoted as $(\text{TiO}_2)_{10}/\text{OTMS}$ hereafter) showed contact angle of $94.5 \pm 1.3^\circ$. While contact angles of bare quartz plates and 10-layer titania-film-coated quartz plates were 15.4 ± 1.0 and $35.9 \pm 2.7^\circ$, respectively. This result indicates that self-assembled silane monolayer imparts increased hydrophobicity to the surface. The structure of the superhydrophobic cellulose material fabricated by deposition of $(\text{TiO}_2)_5/\text{OTMS}$ nanocoating on the cellulose nanofiber surface of filter paper is schematically illustrated in Scheme 1. Five-layer thin titania film (thickness ca. 2.5 nm) was first coated onto each cellulose nanofiber surface by surface sol-gel process according to our previous report,^{14a} and successively self-assembled OTMS monolayer was deposited onto the titania film surface by solution immersion, forming the outermost layer of the coating (see Supporting Information for experimental details).¹⁵

Contact angle of the native filter paper could not be measured due to its natural superhydrophilic character, while contact angle of filter paper coated with 5-layer ultrathin titania films was measured to be $57.5 \pm 6.5^\circ$. This is because the dense titania coating prevented the contact between the water droplets and the cellulose fiber surface. After further deposition of the OTMS monolayer, the contact angle was dramatically increased to be $154.8 \pm 1.5^\circ$ (Figure 1, inset).

The wetting behavior of the resulting superhydrophobic filter paper can be explained by the Cassie–Baxter equation. It was found that air occupies 89.7% of the contact area between the water droplet and the modified filter paper surface. Filter paper is composed of cellulose microfibrils with interspaces between them. These interspaces capture a lot of air to reduce the water/solid contact area, which can effectively enhance the hydrophobicity. The obtained superhydrophobic cellulose material is of excellent long-term stability. The contact angles remained essentially constant even after storing in air for as long as eighteen months.

Figure 1 represents the contact angles of droplets with varied pH values on the superhydrophobic filter paper, showing that the contact angles (over 150°) exhibit no obvious change

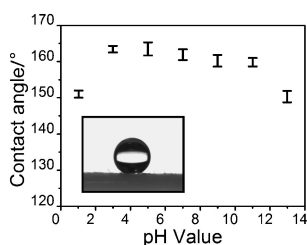


Figure 1. Contact angle measurement of droplets with different pH values on the surface of the superhydrophobic filter paper. The inset shows the photograph of water droplet placed on the surface.

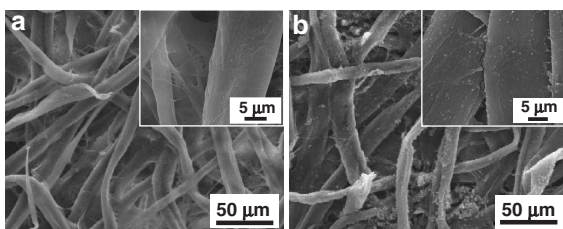


Figure 2. FE-SEM images of bare filter paper (a) and filter paper modified with ultrathin $(\text{TiO}_2)_5/\text{OTMS}$ film.

within experimental error over the pH range from 3.0 to 11.0, while decrease appreciably only with strong acidic (pH 1.0) and strong basic (pH 13.0) droplets.

The resultant superhydrophobic filter papers still displayed a prominent durability with contact angle higher than 148° after immersing in aqueous solutions with pH from 3.0 to 11.0 for 48 h. However, the contact angles changed to 149.8 ± 1.5 and $149.3 \pm 0.9^\circ$ in strong acid (pH 1.0) solution for 24 and 48 h immersion, respectively; whereas in strong basic (pH 13.0) solution, the contact angles reduced to $145.6 \pm 0.4^\circ$ for 24 h immersion and decreased dramatically to $130.6 \pm 1.7^\circ$ for 48 h immersion. The superhydrophobicity of the resultant hydrophobic filter paper was impaired in these cases, which was mainly because titania film and silane monolayer were dissolved in strong acidic (pH 1.0) and strong basic (pH 13.0) solution, respectively.

The morphology of the filter paper coated with $(\text{TiO}_2)_5/\text{OTMS}$ nanocoating was characterized by field emission scanning electron microscopy (FE-SEM). Figure 2a shows that the bare filter paper is composed of cross-linked cellulose microfibrils, and Figure 2b reveals that ultrathin $(\text{TiO}_2)_5/\text{OTMS}$ nanocoating appears have no obvious deleterious effects on the original structures and morphologies of the native filter paper. Moreover, it is notable that the corresponding physical properties of the original filter paper such as flexibility and mechanical properties are well retained after the modification with ultrathin titania/OTMS film.

The precoating ultrathin titania film plays a key role in the fabrication of the superhydrophobic cellulose materials here. Control experiment showed that OTMS monolayer could not be directly deposited onto the cellulose fiber surface without the titania precoating at room temperature, implying that the titania nanocoating provides an essential platform for further assembly of silane monolayer. Similar self-assembly was readily applicable to other cellulose materials, such as cotton, to obtain the superhydrophobic counter material.¹⁵

Table 1. Contact angle ($^\circ$) for filter paper modified with thin titania films with different thickness (d) and different long alkyl chain silanes

	5-L titania ($d \approx 2.5$ nm)	10-L titania ($d \approx 5$ nm)	20-L titania ($d \approx 10$ nm)
$(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_3$	154.6 ± 1.3	151.9 ± 1.5	152.8 ± 1.0
$(\text{MeO})_3\text{SiCH}_2(\text{CH}_2)_6\text{CH}_3$	154.8 ± 1.5	160.5 ± 1.0	158.2 ± 0.7
$(\text{MeO})_3\text{SiCH}_2(\text{CH}_2)_{16}\text{CH}_3$	159.6 ± 0.9	151.0 ± 0.8	154.7 ± 1.2

To evaluate the effect of alkyl chain length of silane molecules and titania film thickness on the superhydrophobicity, silanes with different length of alkyl chain were deposited onto ultrathin titania film (with different thickness of ca. 2.5 nm, 5 and 10 nm) precoated nanofiber surfaces of filter paper to obtain superhydrophobic cellulose materials, and the results are summarized in Table 1. Contact angles of all the resultant hydrophobic filter papers are higher than 150° , displaying excellent superhydrophobicity. It was observed that the alkyl chain length of silanes and the thickness of titania film seemed to have no obvious influence on the superhydrophobicity. It is worthy of note that the ultrathin titania film with only ca. 2.5 nm thickness is good enough to make it possible to fully cover the surface of cellulose nanofibers and for further surface modification.

In summary, we have developed a facile, effective, and low-cost methodology to transform extremely hydrophilic natural cellulose into superhydrophobic material with satisfactory long-term stability, which was achieved by the combination of titania nanocoating and successive deposition of self-assembled alkyl-silane monolayer. This facile process could provide new opportunities to the fabrication of novel superhydrophobic cellulose-based materials.

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- Supporting Information is available electronically on the CSJ-Journal Website, <http://www.csj.jp/journals/chem-lett/index.html>.