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Fabrication of a glass substrate with dual functions of self-cleaning and photocatalytic depollution

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A prototype window glass having two functions of self-cleaning and photocatalytic degradation is fabricated by coating a TiO_2 thin film on one side and silica nanostructures on the other side of a glass substrate. First, a TiO_2 thin film of submicron thickness is coated on one side of a clean glass substrate by immersing in an alcoholic solution of TiO_2 precursor. After TiO_2 film formation, the glass slide is then dipped in an alcoholic solution of silica precursor to coat silica nanostructures on the other side by a sol-gel reaction. During the fabrication process, UV-curable adhesive films are properly attached on the virgin side and the TiO_2 side in turn for protection purpose. The self-cleaning function of the glass substrate is characterized by measuring contact angle and water cleaning power on the silica side, and its photocatalytic depollution function is characterized by estimating decomposition rate of dye molecules on the TiO_2 side in an aqueous solution under UV irradiation. As results, the fabricated coatings are found to have characteristics of self-cleaning close to superhydrophobic surface and good photocatalytic depollution.

Key words: Silica nanostructures, Titania thin film, Sol-gel reaction, Self-cleaning, Photocatalytic depollution.

Introduction

Multifunctional coatings for window glasses of buildings and cars can optimize comfortableness in indoor spaces by controlling environmental conditions inside and outside properly [1]. During the last decades, several types of glass coatings have been developed and commercialized [2], and they are mainly used to improve transmittance (antireflective coatings), thermal transmittance (low-E coatings), solar factor (solar control filters) and glass maintenance (self-cleaning coatings). Nowadays, the glass coatings are widely used in more than 70% of the glass globally produced for a variety of purposes [3].

The self-cleaning coatings have a great potential because of their wide range of possible applications from window glasses to textiles, and their advantageous characteristics of labor-saving and sustainability. For the function of self-cleaning, two approaches have been used: superhydrophobic and superhydrophilic surfaces. Both approaches utilize the action of water to keep surface clean, however they differ in detailed actions: the former by rolling droplets and the latter by sheeting water carrying away dirt [4]. The superhydrophobic surface approach takes advantages of high water contact angles to get the self-cleaning action: on the surfaces water forms almost spherical droplets that readily roll away carrying dust and dirt with them. Basically this

approach requires a surface which has a proper surface roughness in micron or submicron scale and a surface coverage of low energy material such as alkyl or fluoroalkyl groups [5, 6]. In practice, most preparation methods in this approach involve harsh chemical treatments, expensive materials like fluoroalkylsilanes and nanotubes [7, 8], and complex procedures [9-12]. Meanwhile the sol-gel method has been proved to be adequate for the fabrication of properly rough surface permitting the self-assembly of nanostructured surfaces with a cheap "bottom-up" approach [13]. TiO₂ photocatalysts under the ultraviolet (UV) irradiation have very strong oxidation power which can decompose most adsorbed organic molecules on their surfaces. In addition, those photocatalysts become completely wet with water when they absorb the UV light. Because of their photocatalytic properties they have been widely utilized as coating materials for building materials [14]. These photocatalytic coatings have been fabricated by the sol-gel method and proved to yield satisfactory performance for depollution under UV irradiation [15].

In this work, we fabricate a prototype window glass with dual functions of self-cleaning and photocatalytic depollution by coating a TiO_2 thin film on one side and silica nanostructures on the other side. In the coating process, UV-curable tapes are properly utilized to protect the other side of surface. The thickness, the morphology, the surface roughness and the hydrophobicity of the fabricated coatings are characterized by proper analysis tools such as alpha stepper, scanning electron microscope, atomic microscope, contact angle measurement, and

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their target functions are properly estimated by the experiments of organic dye degradation and self-cleaning.

Experimental Details

A glass substrate (soda lime glass slide, Paul Marienfeld GmbH) was cleaned in the Piranha solution $(H_2SO_4: H_2O_2 = 3: 1)$ and dried at 110 °C for more than 2 h. The fabrication procedure of dual function coatings roughly comprises of two stages of TiO₂ coating and SiO₂ hybrid coating. First, a TiO₂ coating solution was prepared by dissolving titanium tetraisopropoxide (TTIP), double distilled water (DW) and acetylacetone (acac) in isopropanol (IPA) (two solutions of different concentration were used; 0.34 M TTIP solution with molar ratio of $[H_2O]/[TTIP] = 5.8$, and 0.1 M TTIP solution with molar ratio of $[H_2O]/[TTIP] = 19.8$). The solution was agitated at room temperature (RT) for 30 min. The acac is known to play a role of stabilizer for the sol-gel reaction by forming Ti(i-PrO)3 acac precursor in which the coordination number of Ti is increased from 4 to 5 [16]. A piece of UV-curable tape (C&A Tech, Korea) was attached to one side of the glass substrate for protection. The glass substrate was coated with a TiO₂ film of submicron thickness by dip-coating it in the coating solution with a dip-coater (Single Vessel DC, KSV). Then the glass substrate was dried at RT for 24 h. The UV-curable tape was detached from the glass substrate after UV irradiation at 240 mW/cm², and the glass was then calcined at 450 °C for 1 h. Second, a SiO₂ coating solution was prepared by dissolving tetraethyl orthosilicate (TEOS), DW and NH_4F in Methanol ([H₂O]/[TEOS] = 7, [NH₄F] = 0.001 M), and agitating the mixture for 30 min. This coating solution was then incubated for a period of time. Another piece of UV-curable tape was attached to TiO₂ coating side for protection. The glass substrate was then coated with a thin film of silica nanoparticles by dip-coating it in the coating solution. After being dried at 80 °C for 1 h, the glass substrate was hydrophobized by a silanization with trimethylchlorosilane (TMCS) in hexane solution. The UV-curable tape was detached from the glass substrate after UV irradiation. Finally the glass substrate with TiO₂ coating and SiO₂ hybrid coating was aged at 125 °C for 1 h. In Fig. 1, the fabrication procedure is illustrated.

The thickness, the morphology and the transmittance of the TiO_2 coating was investigated using an alpha stepper (KLA-Tencor, D-100), a scanning electron

Table 1. Composition of TiO₂ coating and SiO₂ hybrid coating.

Coating	Composition
TiO ₂	TTIP = 0.1 M, [H ₂ O]/[TTIP] = 19.8, TTIP = 0.34 M, [H ₂ O]/[TTIP] = 19.8 in IPA
SiO_2	$[H_2O]/[TEOS] = 7$, $[NH_4F] = 0.001$ M in MeOH



Fig. 1. Illustration of fabrication procedure.

microscope (SEM, Hitachi, S-4700) and a UV-vis spectrometer (Perkin Elmer, Lambda 25), respectively. The photocatalytic activity was estimated by measuring degradation rate of methylene blue (MB) dye. An aqueous solution of the dye was prepared at 10 µM, and poured in a large reaction vessel positioned on the top of UV lamp (UVITEC, LF-215LS). The dye concentration was monitored as a function of time using the UV-vis spectrometer (Perkin Elmer, Lambda 25). The hydrophobicity of the silica coating was estimated by measuring contact angle of water droplet (Krüss, DSA 100). The surface roughness was measured using an AFM (Digital Instrument, Nanoman II). To estimate the self-cleaning function of the SiO₂ coating, small amount of carbon black powder (0.1 g) was spread on the flat coating surface, and it was then removed by standing it upright. The remaining carbon black was washed by spreading 1 ml water, and the residual amount of carbon black was estimated.

Results and Discussion

In the process of coating one side of the glass substrate with TiO_2 or SiO_2 film by a sol-gel method, the other side was protected by attaching a UV-curable tape which has been used to transfer silicon wafers in the semiconductor industry. This approach was based on the fact that the UV-curable tape leaves no detectable amount of residue on a silicon wafer surface after it is detached from the surface with UV irradiation at 240 mW/cm². In this study, the fact has been assured from the SEM analysis of the glass surface before attachment and after detachment of the tape.

The thickness of TiO₂ coating was measured to be c.a. $110(\pm 10)$ nm when TTIP concentration was 0.1 M and c.a. $300(\pm 15)$ nm when 0.34 M. Fig. 2 shows the morphologies of the TiO₂ coatings of two different concentrations of TTIP. The coating of 0.1 M TTIP appeared to be pretty dense film comprising interconnected structure of TiO₂ nanoparticles of about $20 \sim 30$ nm. A similar structure was observed with the coating of 0.34 M TTIP. Apparently, both structures seem to have mesopores. As shown in Fig. 3, the light transmittance





Fig. 2. SEM photographs of TiO_2 coatings (a) TTIP concentration = 0.1 M (b) TTIP concentration = 0.34 M.



Fig. 3. Transmittance of TiO₂ coatings.

of TiO₂ coating was estimated to be approximately 92% and 80% for 0.1 M and 0.34 M TTIP coatings, respectively. Fig. 4 shows the photocatalytic activity of the TiO₂ coatings. For 0.1 M precursor, the MB concentration decreased as much as about 27% after 30 min, and about 30% up to 6 h. For 0.34 M precursor, about 65% of MB was degraded at 30 min and more than about 90% at 6 h. From the results of low and high concentration TTIP, the photocatalytic activity is apparently proportional to film thickness.



Fig. 4. Photocatalytic activity of TiO₂ coatings.





Fig. 5. Contact angles of SiO_2 hybrid coating (a) 128.2 ° for condition A (deposition time 36 h at 40 °C) (b) 130.0 ° for condition B (deposition time 44 h at 40 °C).

When a TiO₂ film absorbs UV light corresponding to the band gap, charge carriers (electrons and holes) are generated, and these carriers cause the photocatalytic properties [17]. The photogenerated holes in the valence band diffuse to the TiO₂ surface and react with adsorbed water molecules, forming hydroxyl radicals. The photogenerated holes and the hydroxyl radicals oxidize nearby organic molecules on the TiO₂ surface. Meanwhile, electrons in the conduction band typically participate in reduction processes, which typically react

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Fig. 6. AFM topography for condition C (deposition 24 h at 25 °C) with surface roughness of c.a. 3.3 nm.





Fig. 7. Comparison of carbon black residue on SiO_2 hybrid coating with that on bare window: (a) with and (b) without the SiO_2 hybrid coating.

with molecular oxygen to produce superoxide radical anions [17]. Therefore, the observed linear relationship between photocatalytic acitivity and film thickness implies that all photons absorbed in the TiO₂ film equivalently generate electron-hole pairs regardless of the depth from the TiO₂ surface, and the pairs are effectively transported to its reaction site [18]. For a TiO₂ film on a soda lime glass (SLG) substrate, it has been reported that a structure of Na_xTiO₂ is formed by Na diffusion near the interface between TiO_2 and SLG, and it lowers photocatalytic activity of thin TiO₂ film less than about 300 nm [18, 19]. However, this was not observed in this study, which indicates the Na diffusion into the interface was insignificant in the fabrication process. Although thicker coating showed higher photocatalytic activity, it has a disadvantage of low transmittance, and thus an optimal thickness presumably exists to compromise transmittance and photocatalytic activity.

Fig. 5 shows the contact angles of water droplets

formed on SiO₂ hybrid coatings fabricated with the deposition times of 36 h and 44 h at 40 °C. The fabricated SiO₂ hybrid coatings with contact angles of 128.2° and 130.0° can be regarded as close to superhydrophobic surface ($\geq 150^{\circ}$). In general, a proper surface roughness and a surface coverage of low energy material are necessary in order for a surface to have superhydrophobicity. Present contact angle results less than 150 ° imply that either surface roughness or low surface energy material does not fulfill the superhydrophobicity. In this study, perfluorooctylsilane (PFOS) was also used and the resulting contact angles were found to be $140 \sim 150^{\circ}$, which are slightly higher than those for TMCS. However PFOS-treated coatings were haze and showed lower transmittance, and turned out to be improper for window application requiring high tramsmittance. Therefore, desirable alternative approach is improvement of surface roughness. Fig. 6 shows the AFM topography of SiO₂ hybrid coating fabricated with the deposition times of 24 h at 25 °C, of which rootmean-square (rms) surface roughness is c.a. 3.3 nm. This surface roughness depends on the deposition time, which varies particle size deposited on to glass substrate [20]. A systematic study regarding the surface roughness effect is needed to accomplish superhrophobicity in the future. In Fig. 7, the self-cleaning experiment result for the glass with hydrophobic coatings is compared with that for the bare glass. As shown in the figure, most of the carbon black pollution spread on the hydrophobic SiO₂ hybrid coating was removed by the simple action of standing it upright (pollution was minimized). Importantly, even small amount of water (1 mL) was then able to wash out most of remaining carbon black pollution, indicating good self-cleaning function.

Conclusions

In this work, a prototype window glass substrate having dual functions of self-cleaning and photocatalytic depollution was fabricated, and from the results of fabrication procedure and characterization revealed the following conclusions:

1. A glass substrate was successfully coated with

 TiO_2 and SiO_2 hybrid films at different side by specific sol-gel reactions using UV-curable tapes properly.

2. The fabricated glass substrate was found to have dual functions of self-cleaning close to superhydrophobic surface and good photocatalytic depollution.

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