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Original Article

Deposition of transparent, hydrophobic polydimethylsiloxane - nanocrystalline TiO_2 hybrid films on glass substrate

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Abstract

Transparent, hydrophobic hybrid films were deposited on glass substrate from solution containing hydroxyl-terminated polydimethylsiloxane (PDMS) and TiO_2 sol by using a dip coating method. The effects of the film heat-treatment temperature and PDMS/TiO_2 component on surface properties of the hybrid films were investigated by water drop contact angle measurement, and by atomic force microscopy (AFM) and scanning electron microscope (SEM) analyses. Surface morphology of the hybrid film changed from smooth surface containing tiny spikes to rougher surface containing large protrusions during heat-treatment temperatures of 60 - 300°C and became smooth surface containing very fine spikes at 500°C, corresponding to a change hydrophobicity behavior from contact angle measurement. The suitable condition for preparation of hydrophobic coating from this current recipe was at the PDMS/TiO_2 volume ratio of 1.00 - 2.33 and heat-treatment temperature of 60°C. All the films were transparent regardless of post heat-treatment temperature. However, the films containing higher content of PDMS were slightly more transparent.

Keywords: hybrid film, hydrophobic, transparent, polydimethylsiloxane, titanium dioxide

1. Introduction

Hydrophobic films have been deposited on surfaces such as glasses and plastics for their water-repellent and anti-adhesion functions (Jeong *et al.*, 2001; Kamitani and Teranishi, 2003; Nakajima, 2004). The organic-inorganic hydrophobic hybrid films prepared from hydroxyl-terminated polydimethylsiloxane (PDMS) and titanium dioxide (TiO_2) have been explored (Iketani *et al.*, 2003; Shidou, 2003; Wu *et al.*, 2006; Shidou, 2004). The organic PDMS is typically used as the hydrophobic constituent due to the following reasons. Firstly, its low surface energy of 16-21 $nN \cdot m^{-1}$ makes it a good candidate for hydrophobic coating. Secondly, terminal hydroxyl groups of the PDMS have advantage of being able to participate in the condensation reaction so that the PDMS is incorporated into the inorganic network to prevent large inorganic precipitation to maintain optical transparency. Finally, main chain of the PDMS ($(Si\text{-}O\text{-}Si)_n$) is resistant to an attack from the photocatalytically active TiO_2, and silane functional group adheres strongly to the glass surface. However, accomplishment of the coating having good properties also depends on synthesis condition, which must be carefully controlled.

In this current work, fabrication of optical transparent of organic-inorganic hybrid films on glass substrate was carried out by using the PDMS and nanocrystalline TiO_2 using a simple dip coating method. The effects of heat-treatment temperature and PDMS/TiO_2 ratio on surface properties and hydrophobicity of the PDMS-based hybrid films were investigated. The surface properties were discussed on the basis of the change of surface topography and water contact angle.

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2. Materials and Methods

2.1 Starting materials

Hydroxyl terminated-PDMS, with an average molecular weight of 4,000 (Aldrich), was used to prepare the PDMS solution. Tetrabutyl orthotitanate ($Ti(OBu)_4$, 97%, Fluka) was used as a precursor for synthesis of the TiO_2 sol. Anhydrous ethanol (99.9%, Mallinckrodt), 1-propanol (Fisher) and de-ionized water were used as solvent. Nitric acid (65%, Scharlau) was used as catalyst for the hydrolysis of the tetrabutyl orthotitanate during the preparation of the TiO_2 sol. Since tetrabutyl orthotitanate is highly sensitive to humidity, the glassware used for TiO_2 sol synthesis was dried before using.

2.2 Preparation of PDMS-TiO_2 hybrid films

The solution for dip coating was prepared by dissolving the hydroxyl terminated-PDMS in 40 mL anhydrous 1-propanol under vigorous ultrasonication until the solution became transparent and then mixed with an appropriate component of 0.4 M TiO_2 sol. The TiO_2 sol was prepared by dissolving tetrabutyl orthotitanate in an absolute ethanol containing small amount of water and nitric acid. The mixing solution between PDMS and TiO_2 sol was vigorously stirred for 30 min. The pH of this precursor solution was 2.0. Before coating, the glass substrates were washed with cleaning agents (ethanol, acetone and de-ionized water, respectively) and then dried at 60°C. The cleaned glass substrates were immersed in the coating solution and slowly withdrawn at a speed of 0.05 mm·min^{-1}. After withdrawing for few minutes, the coated substrates were re-immersed in the coating solution and subsequently withdrawn at the same speed as used in the first layer. Finally, the coated glass substrates were dried in the oven at 60°C, and then heat treated at 100, 300 and 500°C. In addition, the volume ratios of the PDMS to TiO_2 were varied in the range of 0.25-4.00. These solutions were coated on the glass slide substrates following the above method and then heat treated at 60°C.

2.2 Characterization

Surface wetting ability of the hybrid films was investigated by contact angle measurement (Ramé-hart Instrument Co.). A droplet of de-ionized water was mounted on the hybrid film surface by using a microsyringe. Image of water droplets on the film surface was recorded using a CCD camera. Then, a curvature profile was created and the contact angle measured. The measurement was conducted on five different areas of the specimen surface.

Surface topography and film thickness were measured by using an atomic force microscopy (AFM, Seiko instrument SPA 400). For topography measurement, a cantilever with a Si tip (NSG01) was used. A sample area of 5 µm x 5 µm was scanned at a scanning rate of 1.0 Hz. Film thicknesses were measured on the films having a PDMS/TiO_2 volume ratio of 0.25 and 4.0 and heat treated at 60°C. The two films were selected since they had the lowest and highest PDMS/TiO_2 volume ratio (Film thickness is dependent on TiO_2 content). A scratch was made across the film to create a step between the film and the substrate, and the film thickness was determined by scanning the AFM tip across the revealed step.

Morphological images of the hybrid film were investigated by using a scanning electron microscope (SEM, Hitachi S-3400N). Film transparency was measured by using a UV-visible spectrophotometer. Nanocrystalline TiO_2 present in the sol before mixing with the PDMS solution was characterized by using a transmission electron microscope (TEM, JEOL JEM-2010).

3. Results and Discussion

The 3-dimensional (3D) topographical mapping image obtained from the AFM analysis for bare glass substrate is shown in Figure 1. The bare glass had uniform surface having a peak to valley value of about 2-3 nm. Such morphology

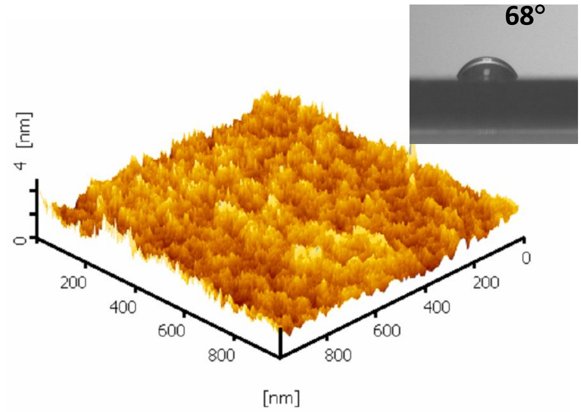

Figure 1. A 3D AFM topographical image of bare glass substrate. The bare surface exhibited water contact angle of 68 degrees.

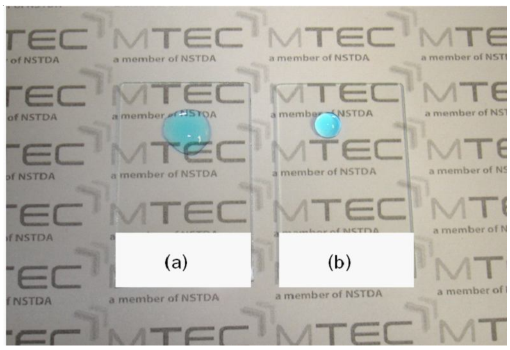

Figure 2. Photograph of (a) bare glass substrate and (b) hybrid film coated-glass substrate. Water droplet beaded up on the hydrophobic surface, while spread up on bare surface.

Table 1. Water contact angle of the hybrid films coated on the glass substrate heat-treated at various temperatures. Volume ratio of the PDMS and TiO_2 in the coating precursor was 2:1.

Heating Temperature (°C)	Contact angle (degree)	RMS surface roughness (nm)
25 (as-prepared)	99	1.3
60	101	2.0
100	96	13.2
300	70	8.9
500	28	2.8

provided water drop contact angle of 68 degrees which is a characteristic of hydrophilic surface. Figure 2 shows an image of bare and coated glass substrates. The precursor solution for dip coating contained PDMS and TiO_2 volume ratio of 2:1. The coated substrate appeared smooth macroscopically and had good optical transparency. After the substrate was ultrasonically cleaned with de-ionized water, the hybrid film still adhered on the substrate.

After coating with the hybrid film, the glass surface became more hydrophobic as the water drop contact angle increased compared to the value obtained from the bare glass substrate. Table 1 summarizes the static contact angles as well as a surface roughness obtained from AFM analysis as a function of heat-treatment temperatures in the range of 60-500°C. A Root Mean Square (RMS) roughness of all films was calculated according to the following equation:

$$RMS = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - Z_{av})^2}{N}} \quad (1)$$

where Z_{av} is the average height for the entire region, Z_i is the height of individual point i, and N is the number of points measured within a given area. According to the data in Table 1, similar contact angle, and hence similar hydrophobicity, was obtained from the as-prepared film and the films heated for up to 100°C. Degree of hydrophobicity decreased with increasing film heat-treatment temperature above 100°C. It should be noted that hydrophobicity as characterized by water contact angle was not entirely governed by surface roughness as previously anticipated. It had been reported that hydrophobicity depended on both surface roughness and the chemical composition that can lower surface energy sufficiently (Eick *et al.*, 1975). In this present work, the PDMS had low surface energy, and therefore was expected to largely attribute to the increase of hydrophobicity. However, at high heat-treatment temperatures, the PDMS was decomposed, resulting in the decrease of the film contact angle.

SEM and AFM results of the hybrid films, shown in Figure 3, revealed the surface morphology change as a function of heat-treatment temperature. Photos of water contact angle are also displayed. SEM image of the as-prepared hybrid film (Figure 3(a)) showed tiny white spots with approx. size of around 200-500 nm uniformly dispersed on the entire surface. The result of AFM analysis of the same specimen revealed smooth surface (RMS roughness = 2.0 nm) and

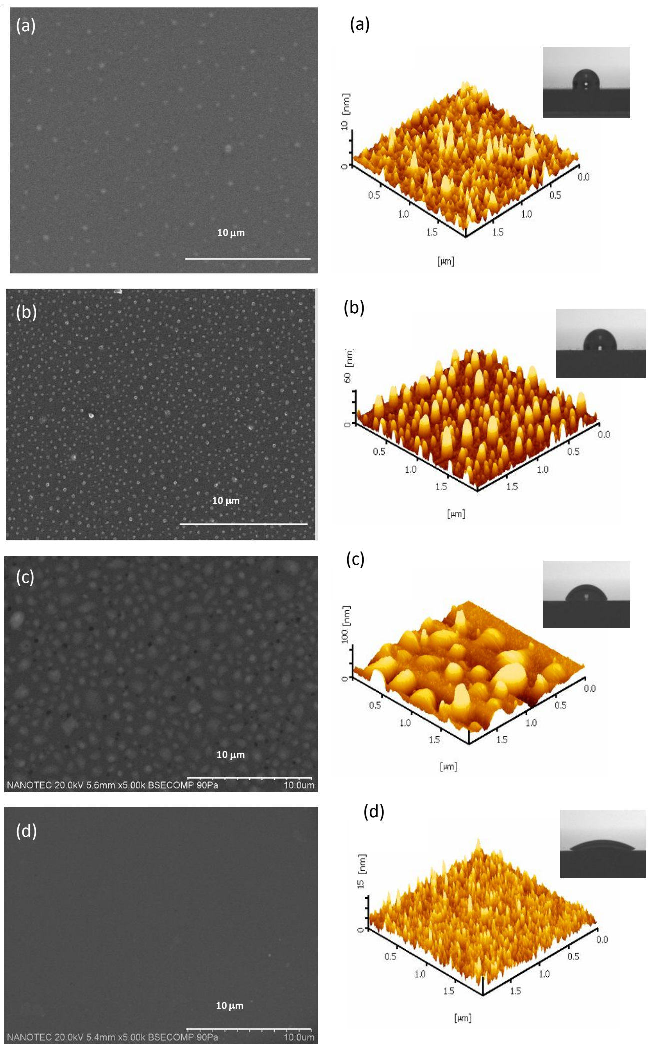

Figure 3. SEM and 3D AFM topographical images of the hybrid films surface on the glass substrate: (a) as-prepared, (b) heated at 100°C, (c) heated at 300°C and (d) heated at 500°C.

contained fine spike of around 100 - 200 nm in size. It was expected that the white spots seen in the SEM image and the spikes seen in the AFM image were titanium oxide compound since such inorganic moiety would give better contrast than an organic one. After heating at 100°C, the surface consisted of densely distributed, very fine white spots appeared as a result of bloating (Figure 3(b)). The AFM result shows protrusions which could arise as a result of solvent evaporation of the PDMS compound. The bloating and also PDMS decomposition became more evident when the specimen was heated at 300°C (Figure 3(c)). The white spots were not observed after heating at 500°C. Only smooth surface containing very fine spikes was observed. At this heat-treatment temperature, the PDMS matrix decomposed resulting in inorganic-like silicon oxide particles which appeared as uniform contrast in the SEM images, and as very fine spikes in the AFM image (Figure 3(d)). It can be drawn from these results that the surface containing more PDMS component as shown in Figures 3(a) and 3(b) tended to yield better hydrophobic property than the surface containing more inorganic component as depicted in Figures 3(c) and 3(d) regardless of the degree of surface roughness.

Relationship between hydrophobicity and the PDMS/TiO_2 volume ratio is summarized in Table 2. The contact angle increased when the PDMS/TiO_2 ratio increased from 0.25 to 0.40 and tended to be constant afterwards. Low contact angle observed at low volume ratio of PDMS/TiO_2 was attributed to low content of the PDMS which had low surface energy, supporting the results described earlier (Figure 3).

Figure 4 shows AFM images of the PDMS-based hybrid surfaces at heat-treatment temperature of 60°C as a function of composition. Different features were observed at various PDMS/TiO_2 compositions. It seemed that there were nanoparticles of TiO_2 covering all over the film surface at low volume ratio of PDMS/TiO_2. We believe that such feature arose as a result of phase separation between the inorganic and organic components or inhomogeneity during mixing of the two precursors. At high volume ratio of PDMS/TiO_2, the films were more homogeneous, perhaps due to better mixing of PDMS and nanocrystalline TiO_2. It should be noted here that although samples (c) and (d) had very smooth surface, they have high degree of hydrophobicity since they contained higher content of the PDMS.

Table 2. Water contact angle of the hybrid films having PDMS/TiO_2 volume ratio of 0.25 - 4.0 at heat-treatment temperature of 60°C.

PDMS/TiO_2 ratio	Contact angle (degree)	Surface roughness, RMS (nm)
0.25	80	5.9
0.40	98	11.4
1.00	103	19.4
2.33	103	4.0
4.00	98	2.7

The thicknesses of the films heat treated at 60°C and having the PDMS/TiO_2 volume ratio of 0.25 and 4.0 were 320±15 and 250±13 nm, respectively. It is clearly observed that the film containing higher TiO_2 content was thicker. The thickness of the film having PDMS/TiO_2 volume ratio between 0.25 and 4.0 should be in a range of 320 and 250 nm.

To further investigate the titanium compound present in the hybrid, the titanium precursor solution prepared by dissolving tetrabutyl orthotitanate in anhydrous ethanol in the presence of small amount of water and nitric acid was subjected to a TEM analysis. It was assumed that the tita-

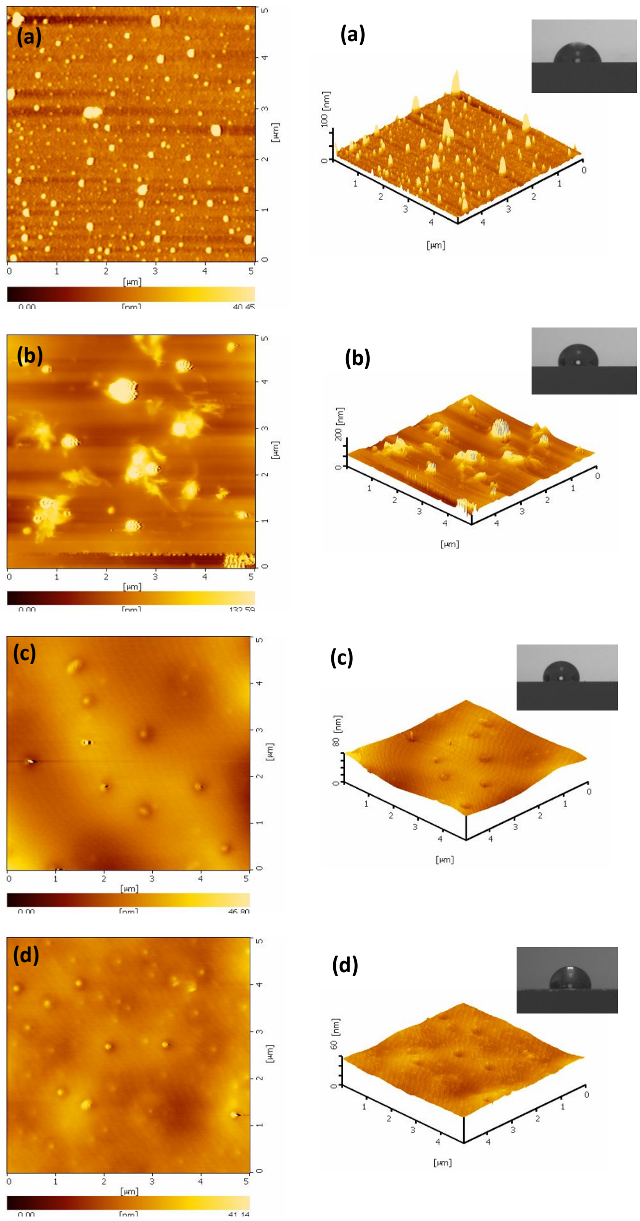

Figure 4. 2D and 3D AFM images of the hybrid surfaces having the PDMS/TiO_2 volume ratio of (a) 0.25, (b) 1.00, (c) 2.33 and (d) 4.00 at heat-treatment temperature of 60°C.

nium compound present in this precursor was similar to that present in the as-prepared hybrid film since the titanium precursor was immediately mixed with the PDMS solution, and no further hydrolysis reaction was expected afterward. A TEM image (Figure 5) of the specimen taken from the titanium alkoxide precursor solution revealed densely packed nanocrystals having crystallite size of approximately 4-6 nm. These nanocrystals were anatase TiO_2 as identified by a selected area electron diffraction pattern (inset, Figure 5). Therefore, it can be confirmed that the white spots seen in SEM image of the as-prepared film (Figure 3(a)) were agglomerates of the TiO_2 nanocrystals.

Figure 6 shows transmission spectra of the hybrid films treated at various temperatures. All the films had light transmission in the range of 85-90%, and were therefore optically transparent. It is not evident that the film's transparency was significantly affected by heat-treatment temperature although chemical composition of the PDMS might have been altered at above 400ºC. Similar range of optical transparency, *i.e.* roughly 85-90%, was observed on films containing various ratios of PDMS and TiO_2 (Figure 7) and heated at 60ºC. However, transparency tended to increase with the PDMS content in the film. This trend is reasonable since the PDMS itself is transparent.

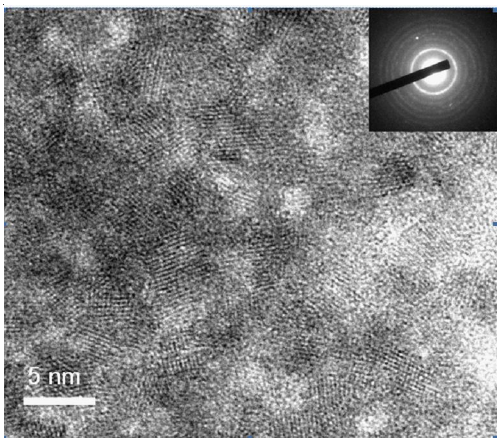

Figure 5. TEM image of the specimen taken from the titanium alkoxide precursor solution. A selected area electron diffraction pattern corresponds to anatase TiO_2.

4. Conclusions

Hydrophobic PDMS-based organic/inorganic hybrid films having good optical transparency had been coated on glass substrate by dip coating method. The TiO_2 moiety had good distribution in the PDMS matrix. Hydrophobicity decreased with the increase of heat-treatment temperature since the film changed from the PDMS base to silica base. High hydrophobic property was obtained from the films having PDMS/TiO_2 higher or equal to 0.4 and heat-treated at 60°C.

Acknowledgements

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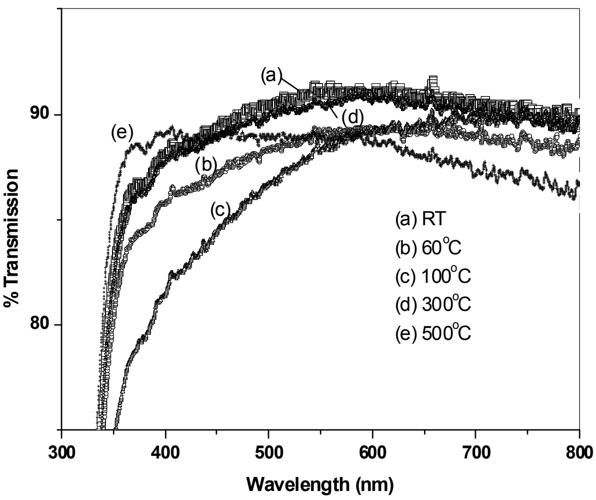

Figure 6. Transmission spectra of the as-prepared hybrid film, and the films heated at 60-500ºC. The films were prepared from the precursor containing volume ratio of PDMS: TiO_2 of 2:1.

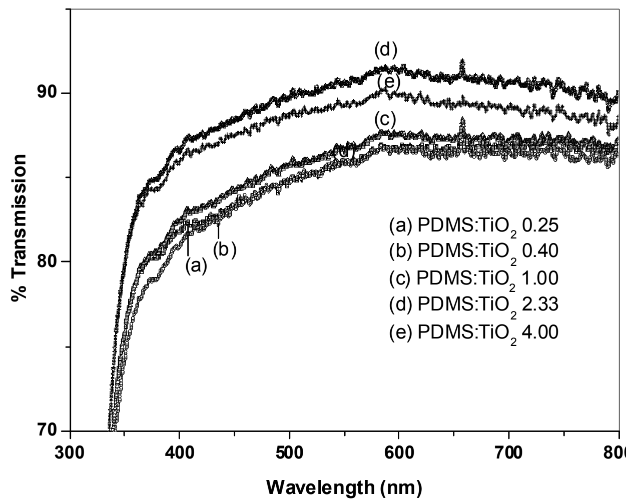

Figure 7. Transmission spectra of as-prepared hybrid films having various ratios of PDMS and TiO_2.

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