TiO₂/silane coupling agent composed of two layers structure: A super-hydrophilic self-cleaning coating applied in PV panels

Hong Zhong, Yan Hu, Yuanhao Wang, Hongxing Yang

Abstract

To improve the properties of anti-dust for PV modules, the concept of self-cleaning has been proposed for many years. However, the traditional self-cleaning coating is unstable in nature environment, which limited its application in the PV panels. Therefore, this study aims to design a novel super-hydrophilic coating with high stability and corrosion resistance, which would be very advantageous to apply in the PV panels. The super-hydrophilic self-cleaning coating is composed of 3-triethoxysilylpropylamine (KH550) and TiO₂. KH550 is a kind of surface modification agent, which creates more active groups on the surface of glasses. TiO₂ is prepared by a hydrothermal reaction with titanium ethoxide, and the influence of pH is investigated as an important factor during the application in PV panels. The composition was measured by UV/VIS/NIR spectrophotometer, and the particle size distribution and the surface structure were characterized by Scanning Electron Microscope (SEM). The TiO₂ nanocrystal was investigated by X-Ray Diffraction (XRD) and Transmission Electron Microscope (TEM). The water contact angle (WCA) was measured by contact angle instrument. It was found that the static water contact angle on the surface of super-hydrophobic coating was as lower than 5°, which show an excellent super-hydrophilic property. Abstract should state the principal results and conclusions briefly, and the significance of this study.

1. Introduction

The application of photovoltaic power station was increased with over 150 gigawatts (GW) capacity in the past 4 years, more than the cumulative installation volume in the previous 4 decades [1]. PV installations have been expected with a great significant for the observed rapid decrease in system prices, the lower cost of capital, and PV’s market maturation. PV installed capacity in the world is likely to be more than doubled in a few years, and PV is installed faster than any other renewable energy technologies [2]. The solar PV panel as the core component of the solar power system remains long-running, so the effect of the dust deposition on the system efficiency is significant. The sources of the dusts include the tiny inorganic particle formed by the motion of sand, soil and wind, the below dust due to the industry, building, and transportation, and organic dust form the biomass of animals and plants [3–5]. The researches about the effect of the dust-fouling on PV panel have been studied for many years all around the world. Due to the different air quality in different area, the effect of the dust-fouling on PV panels are quite different. In dry and less...
rainfall area, the dust has a great effect on efficiency of the PV panels. Nimmo and Said [6] discovered that a reduction of efficiency reaches 26%–40% in Saudi Arabia after 6 month without washing. Sayigh [7] showed another result that the efficiency of solar thermal collector decreased 30% after 3 days without washing. In 1981, Wakin proposed that 17% of efficiency degradation for the PV panel occurred after 6 days in Kuwait. EI-Nashar, [8] who comes from The United Arab Emirates showed that the transmittance of glass reduced 70% because of the dust in summer.

Conventional cleaning methods involving sanitizing materials and solutions are necessary to maintain the freshness of the surface of PV panels. Besides of the economic burden, extensive cleaning potentially leads hazardous substances to the environment and ecosystem. Inspired by the surfaces with a high intrinsic ability to clean themselves in nature, the self-cleaning surface, has attracted huge research curiosity in past decades due to its unique mechanism and high adaptability [9–14]. The concept of self-cleaning was based on the super-hydrophobic or super-hydrophilic nature of certain plant leaves. The most well-known example for super-hydrophobic is the lotus leaf, which allows the water droplets rolling off the surface with dirt to obtain a cleaning surface. This surface, as shown in Fig. 1, demonstrates a water contact angle (WCA) higher/larger? than 150° and a small water sliding angle lower/smaller? than 2°. On the contrary, water film can be formed on a super-hydrophilic surface to detach the dirt components from substrate. As show in Fig. 2, the WCA is extremely small or even zero and the water film makes the dirt components movable along with the water flow on the surface. Thus, both super-hydrophobic [15–18] and super-hydrophilic surface [19–20] can be efficiently cleaned only with the aid of water.

In generally, super-hydrophobic surfaces are composited by some organic materials with micro- and nano-structure. However, most of the super-hydrophobic surfaces will fail, when they are exposed in the air. Because they would be damaged by some environmental factors which include chemical reaction with some solution and air, ultraviolet aging, erosion by some particles and germs, even mechanical wear, which limit the application of the super-hydrophobic coating in PV panels.

Most of super-hydrophilic self-cleaning coatings are composited of TiO2 which is a kind of photocatalyst [12]. These coatings can chemically break down dirt when exposed to light. However, with the poor dispersion and adhesion, this coating show a short life time and low transmittance. Despite the commercialization of a hydrophilic self-cleaning coating in a few products, the field is far from mature. Also, there are many other materials to process a super-hydrophilic surface. Hu Yan [6] showed a controllable water contact angle of super-hydrophilic coating with TEOS and silane coupling agent. But the lifetime of this coating is not long enough which limited its application in the PV panels.

2. Experiment

2.1. Nanosized TiO2 synthesis

Nanosized anatase TiO2 was prepared by the following route and the structures of raw materials was shown in Fig. 3. Titanium ethoxide (30 ml, Ti 7.3 wt.%) (guaranteed reagent grade from Alfa-Aesar) was diluted with absolute ethyl alcohol (100 ml) under vigorous stirring. After rotary evaporation, the pale brown colloid was obtained, then the hydrochloric acid (36%) and nitric acid (60%)
were added as the cooperative acid catalyst, whose pH was 3. The mixed liquid was heated at 70 °C for 3 h and then autoclaved in a Teflon-lined autoclave at 160 °C for 8 h. After dyeing at 80 °C in a dyeing oven, nano-sized TiO2 was obtained. The preparation process of TiO2 was shown in Fig. 4. The autoclaved and dry samples are denoted as Ax, where x is the sample number corresponding to the different preparation conditions. The preparation conditions of the samples are listed in Table 1.

### 2.2. Coating procedure

The glass sheets (1 × 1.5 cm²) were cleaned with cleaning compounds instead of PV panels. The substrates were loaded on the stage after the plasma treatment (PT-2S, Shenzhen Sanhe Mechanical & Electric Science and Technology Co., LTD, China), then a layer of KH550 was deposited on the surface of the glass sheets by pulling method (Fig. 5). The TiO2 coating was prepared with deionized water and absolute ethyl alcohol (H2O:C2H5OH = 7:3). The bluish coating appeared from the apex of the nozzle when injecting the working gas and applying power. The coating scanned the whole area of the substrates with identical scanning rates (0.5 s cm⁻²), forming a transparent layer on the surface (Fig. 6).

### 2.3. Characterization

The crystallinity of the TiO2 samples were checked by powder X-ray diffraction (XRD) (Bruker D8 Advance, Germany) at 50 kV and 150 mA by scanning at 5° 2θ min⁻¹. The morphology and the

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>HCl</th>
<th>HNO3</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>/</td>
<td>/</td>
<td>5.73</td>
</tr>
<tr>
<td>A2</td>
<td>0.12</td>
<td>0.26</td>
<td>1.74</td>
</tr>
<tr>
<td>A3</td>
<td>0.12</td>
<td>0.69</td>
<td>0.78</td>
</tr>
<tr>
<td>A4</td>
<td>0.12</td>
<td>1.38</td>
<td>0.34</td>
</tr>
<tr>
<td>A5</td>
<td>0.12</td>
<td>1.58</td>
<td>0.30</td>
</tr>
<tr>
<td>A6</td>
<td>0.12</td>
<td>2.76</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Fig. 4. The synthetic process of the TiO2.

Fig. 5. The glass sheet treated by KH550.

Fig. 6. The glass sheet coated by TiO2.
size of TiO₂ nano-crystallites were investigated by high resolution transmission electron microscopy (HRTEM) with a JEM Model JEM-2011 electron microscope. At the same time, electron diffraction analysis was carried out to determine the crystal phase of the nano-crystallites. The TEM sample was prepared by ultrasonic dispersed TiO₂ ethanol solution onto a copper grid covered with a thin carbon layer. The dispersion of TiO₂ samples were investigated by laser particle analyzer with a Malvern 3000.

The static water contact angle (WCA) on the as-prepared samples were measured from sessile drops by a contact angle meter equipped with a stage (JCY20-13, Shanghai Fangrui Science & Technology Co., LTD, China), and the full spectrum transmittance of coating was measured by UV/VIS/NIR spectrophotometer with a HITACHI U-4100.

2.4. Measurement of PV panels output with coating

Analysis of the PV panels output is the key step to understand what effects will be brought by coating TiO₂ layer. To estimate the energy output, additional spectral conditions must be examined. PV panels were firstly divided into several groups and the deviation of the output for these groups was lower than 0.5%. The PV panels were firstly sprayed by KH550 ethanol solution (1%) with a nozzle in 0.5 mm of bore, and KH550 scanned the whole area of the surface of PV panels with identical scanning rates (0.1 s cm⁻²), and dry at room temperature. After that, TiO₂ colloidal solution was sprayed on the surface of PV panels by the same method. Each group of PV panels ware was installed on the roof of building, and daily power generation of the coated PV panels and normal PV panels were collected, respectively.

3. Results and discussions

3.1. Synthesis of TiO₂ nanocrystals

Fig. 7 presents XRD patterns of TiO₂ nanocrystals (A1) prepared by hydrothermal process, and the prepared TiO₂ nanocrystals was
anatase form. The XRD pattern of A1 did not show any other crystal characteristics, which observed for the standard samples of pure TiO$_2$ nanocrystals.

Deionized water/ethyl alcohol was used as the solvent to disperse the TiO$_2$ and reduce its aggregation. HTEM test of the TiO$_2$ colloid solvent is shown in Fig. 8. The average primary particle size of TiO$_2$ is 5 nm (Fig. 8a). Radius of diffractions circle (Fig. 8b) and interplanar crystal spacing (Fig. 8c) of A1 shows the feature of crystal faces (101, 004, 200) for TiO$_2$, which further confirmed the identity of the TiO$_2$.

Fig. 9 shows the secondary particle size distribution in the water, which can be used as a measure of the TiO$_2$ dispersion. The secondary particle size means the aggregate nanoparticles in dispersion phase, and low average secondary particle size means high dispersion. The left image of Fig. 9 shows the transparent TiO$_2$ coating, which is a kind of bluish coating without precipitate. The narrow size distribution was found from 12 nm to 30 nm, and the average of the secondary particle size is only 19 nm, which further confirmed a high dispersion of TiO$_2$.

3.2. Effect of acid

Fig. 10 shows the XRD spectrum of different samples, and the XRD pattern of A1 show the clear spectral characteristics for TiO$_2$ which confirmed the identity of TiO$_2$. By calculating the peak intensity from the XRD data, it clearly shows that the peak intensity of [101] direction increases with the decrease of pH. The peak intensity of [101] is always as a measure of the degree of crystallinity for TiO$_2$. Thus, with the decreasing pH, the crystallinity of TiO$_2$ increased, which means the photocatalyst property will be improved.

Fig. 11 shows the optical property of TiO$_2$ coating. The samples were prepared with KH550 and TiO$_2$ coating by spraying method, and the TiO$_2$ contents in all samples were 1%. Before the test, these specimens were drying at room temperature. Because the band gap of TiO$_2$ is around 3.2 eV, all the samples had a light absorption in UV region, which can induce the generation of hydroxyl radical (−OH) and superoxide anion (O$_3^-$) to break down organic dirt and obtain a super-hydrophilic surface. But a lower absorption in visible light region as shown in Fig. 11 may be a negative effect that needs to be considered.

<table>
<thead>
<tr>
<th>Sample</th>
<th>UV-light</th>
<th>Visible light</th>
<th>IR light</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.8%</td>
<td>0.1%</td>
<td>0%</td>
</tr>
<tr>
<td>A2</td>
<td>1.3%</td>
<td>0.2%</td>
<td>0%</td>
</tr>
<tr>
<td>A3</td>
<td>4.3%</td>
<td>0.9%</td>
<td>0.2%</td>
</tr>
<tr>
<td>A4</td>
<td>6.7%</td>
<td>1.2%</td>
<td>0.5%</td>
</tr>
<tr>
<td>A5</td>
<td>12.4%</td>
<td>2.5%</td>
<td>3.8%</td>
</tr>
<tr>
<td>A6</td>
<td>15.1%</td>
<td>3.3%</td>
<td>6.8%</td>
</tr>
</tbody>
</table>

Table 2: Transmittance reduction of different samples.

Fig. 10. XRD Test for Am.

Fig. 11. Optical properties of different TiO$_2$ samples.
on PV panels output. With the pH decreasing, light absorption increased accordingly due to the enhanced crystallization for TiO$_2$ by more acid in the thermal reaction, which means more anatase TiO$_2$ was obtained. By calculating the area of different samples transmittance, the light transmittance reductions of different samples in different range are shown in Table 2.

According to the data of transmittance reduction for A3 to A6, the visible light and IR light transmittance were reduced with decreased pH, which may be caused by low dispersion of the TiO$_2$ coating.

To evaluate the self-cleaning properties of different samples, a camera was used to record the static behavior of a water droplet on the surface of different samples. As shown in Fig. 12, side view images showed that WCA on the original glass was about 43.7°, and the WCA on the treated surface was lower than 10°. With the decrease of pH, the WCA of the glass with TiO$_2$ coating was diminution, because the degree of crystallization (crystallinity) for TiO$_2$ was enhanced by the addition of acid, which means the self-cleaning property was improved. Thus, a low pH has a positive effect on the output of PV panels. In conclusion, the balance of pH in hydrothermal reaction should be investigated, and an optimum pH value should be obtained when this TiO$_2$ coating is applied in PV panels.

3.3. Applied in PV panels

To investigate the application of the TiO$_2$ coating in PV panels, an outdoor test was prepared in July 2016, Wuyi, China. The daily temperature was recorded as shown in Fig. 13. The average temperature was 32°C and the PM 2.5 and PM 10 were 52 and 108, respectively. The wind direction was north and the accumulative rainfall exceeded 350 mm within the whole month. All the photovoltaic arrays are calibration before test and these PV arrays are in same environment on the roof of buildings.

The PV panel with TiO$_2$ layer is shown in Fig. 14a, which demonstrate a high transmittance of light. The PV arrays with TiO$_2$ coating is shown in Fig. 14b, which is on the roof of buildings without shelter. The solar glass with TiO$_2$ coating is shown in Fig. 14d, and a uniform layer is observed on the surface of the substrate which is consist of low particle size of TiO$_2$. 

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**Fig. 12.** The WCA test for different samples.

**Fig. 13.** The Daily temperature of Wuyi, China.

**Fig. 14.** a: PV panel with TiO$_2$ coating; b: PV arrays with TiO$_2$ coating; c: Original solar glass; d: Solar glass with TiO$_2$ coating.
Considering the effect of pH on the self-cleaning property and light blocking rate, A2, A3 and A4 were employed as the raw materials to prepare the TiO2 coating respectively. The daily generated power was collected and shown in Fig. 15. It is obvious that daily power generation of treated panels were higher than that of the original panels. But at the beginning, the generated power of original panels was higher than A4, the main reason is that the negative effect of the pH plays a dominant role. With over time, benefiting from the positive of high self-cleaning property, the power generation of A4 was higher than others, especially in the last few days of the first month. For the sample A2 and A3, although the power generation of the latter was higher than the former, they were almost the same in the end of the first month. In aggregate, the enhancement of A2 was about 3.2%, A3 was about 3.5% and A4 was about 4.2%.

4. Conclusions

In summary, the super-hydrophilic coating was obtained by KH550 and titanium ethoxide, and the glass sheet coated with these two layers shows a lower WCA and a good transmittance.

The pH during hydrothermal reaction was controlled by the concentrations of hydrochloric acid and nitric acid. With the decrease of pH, the photocatalytic property of TiO2 coating was increased which could enhance the self-cleaning property. But in the meanwhile, the dispersion of TiO2 coating was decreased as well, which could block the light transmittance. Thus, the balance of the pH in hydrothermal reaction should be investigated when the TiO2 coating applied in PV panels.

In Wuyi, the energy production of PV panels can be increased by maximum 4.3% in the first month by using the super-hydrophilic coating with the pH value of 0.34. In this paper, a simple way to obtain the super-hydrophilic coating is developed, and it can be deposited on the surface of PV panels by spraying method for large scale application. Moreover, this super-hydrophilic coating can be applied in curtain wall and auto glass.

Acknowledgements

This study was supported by a research grant from CII-PolyU Innovation Funding Scheme. Great help from the Materials Research Centre and Department of Building Services Engineering of The Hong Kong Polytechnic University is appreciated.

References
