

*Original Article*

# Sol-gel self cleaning superhydrophobic nanocoating for glass surface of solar cell

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**Abstract**

Thin film sol-gel coatings on glass substrates for use in solar cells were studied. The precursor solution was made of tetraethoxyorthosilicate (TEOS 2.0-6.0% v/v) using hexadecyltrimethoxysilane (HDTMS 0.1-1.5% v/v) as hydrophobic modifier in the presence of  $\text{NH}_4\text{OH}$  (0.05-1.0% v/v) as catalyst. Dip-coating was applied to glass and studied for the effects of sol preparation on water-contact angle, transmittance, and resistance to outdoor exposure of the coating. The results showed TEOS, HDTMS and  $\text{NH}_4\text{OH}$  contents at 6.0, 1.0 and 1.0 vol.%, respectively, as optimal. Superhydrophobicity with a water-contact angle of  $150.69^\circ$  can be achieved with high transmittance and self-cleaning properties. The morphology and surface roughness were characterized by AFM and showed aggregates of silica particles in combination with the inherent microscale roughness of glass. The stable voltage of solar cells having a coatings of this type (dip-coating in sol-gel with  $\text{NH}_4\text{OH}$  catalyst) meets the industrial requirements with potential for outdoor applications.

**Keywords:** sol-gel, solar cell, nanotechnology, superhydrophobic, dip-coating

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**1. Introduction**

The development of technologies for renewable energy is essential in the current world scenario that presents environmental problems and eventual shortage of fossil fuel resources. The photovoltaic (PV) technologies stand out because they are renewable, safe, and ecofriendly sources of electrical power (Soklič, Tasbihi, Kete, & Štancar, 2015). Nowadays, in order to increase PV energy production, the technological efforts are driven not only towards the development of high PV performance and reliable solar cells, but also towards mitigating the external effects that can degrade the conversion efficiency of PV modules. One of these external factors is the soiling effect caused by dust accumulation on module surfaces, which reduces the transparency of PV cover glass over time and consequently decreases the energy production (Maghami *et al.*, 2016). Self-

cleaning technology has been developed in the form of a superhydrophobic nanoscopic surface coatings to keep the glass surfaces of solar cells clean and provide a water resistant coating on vehicle windows (Chen *et al.*, 2012). In industrial applications this can reduce labor costs, extend a material's durability, and provide environmental benefits. Therefore, a superhydrophobic solar cell coating was carefully formulated using commercially available low-cost materials.

Nanotechnology can be based on colloidal sol-gel materials, and are specially formulated solutions self-assembled into a monolayer with a nanostructure forming a superhydrophobic surface. Utilizing sol-gel chemistry is a well-known approach to generate inorganic nanophases within an organic matrix (Brinker & Scherer, 1990). The wet chemical sol-gels make it possible to use spraying, wiping, atomizing or dipping to coat a surface. Glass can become self-cleaning with such wet coating. Typically, silicon, titanium, aluminum, and zirconium metal alkoxides are used as inorganic sol-gel precursors. The hydrolysis and condensation reactions are controlled by selection of pH, solvent, water to alkoxide ratio, concentrations of the reactants, type of catalyst, temperature, and reaction time.

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An aqueous primer solution containing a silane coupling agent is used to facilitate adhesion of a polymer to glass surface. Tetraethylorthosilicate (TEOS) and hexadecyltrimethoxysilane (HDTMS) are silane coupling agents that react with functional groups of the polymer, and also can react with free hydroxyl groups on substrate surface. A uniform dispersion on the surface of a nonporous substrate forms an ultrathin layer that is adhesively bridged. Sol-gel silica AR coatings can be prepared from base-catalyzed silica sol, and such antireflective coatings possess almost 100% transmittance (Zhang *et al.*, 2010). The base-catalyzed silica AR coatings using  $\text{NH}_4\text{OH}$  possess high transmittance, which has attracted much attention due to their advantages of low cost, simple coating process, and controllable microstructure (Uhlmann, Suratwara, Davidson, Boulton, & Teowee, 1997). However, by adding hydrocarbon groups such as alkyl or polydimethylsiloxane functional groups one could tune the hydrophobicity of nanosilica coating (Yokogawa *et al.*, 1996).

In this paper, the superhydrophobic self-cleaning properties and surface morphology of coated surfaces are investigated. TEOS and HDTMS as silane coupling agents are used to facilitate adhesion of polymer coatings on glass substrates. Surface modification of nanoparticles was used to achieve extreme superhydrophobicity by dip-coating. Water-contact angles on the coated glass surfaces were assessed for the effects of TEOS, HDTMS and  $\text{NH}_4\text{OH}$  concentrations in the sol preparation steps. Additionally, transmittance and roughness of the surfaces were studied, as measures of performance. The optical stability of the sol-gel coatings were monitored for self-cleaning behavior by measuring the voltage of solar cells with these coatings for 1 month.

## 2. Materials and methods

### 2.1 Materials

Ethanol )95%(, ammonium hydroxide )28%(, tetraethoxysilane )TEOS( and hexadecyltrimethoxysilane )HDTMS( were purchased from U & V Holding )THAILAND( Co., Ltd. All these materials were used as received without any further purification. Deionized water was used throughout the experiments.

### 2.2 Preparation of glass

The glass substrate was cleaned by acetone to wash away colorless chemicals attached to the glass, ethanol to clear the electric poles on the surface, and deionized water to clear off further residues on the glass, in an ultrasonic cleaning bath for 10 min each sequentially. Then the substrate was dried at  $110^\circ\text{C}$  in an oven, prior to dip-coating.

### 2.3 Preparation of sol

The coating substrates were prepared by mixing TEOS )2, 4, or 6% v/v(, HDTMS )0.1, 0.5, 1, or 1.5 v/v(, and ethanol. The solution was left in a closed glass container and stirred at 100 rpm for 30 min. Then 0.5 ml of the  $\text{NH}_4\text{OH}$  catalyst was added (0.05, 0.1, 0.5, or 1.0 )v/v( and the mixture was stirred for 2 hours before use to deposit coatings.

The material was dip-coated onto glass surfaces and the coatings were dried in an oven at  $120^\circ\text{C}$ , as shown in Figure 1.

## 2.4 Characterizations

Optical transmittance spectra of the coated glasses were measured with a UV/VIS Spectrophotometer )Hitachi U-4100( at room temperature. The arithmetic mean of transmittances across wavelengths from 250 to 850 nm is reported as the transmittance %T, showing the antireflective coating effect (ARC). The surface roughness of the films was examined using atomic force microscopy )Icon AFM(. Surface contact angles were determined with water )Contact Angle Goniometer(. Surface morphology of the nanosilica layer and its thickness analysis were investigated using scanning electron microscopy (SEM, FEI Inspect-S50).

## 2.5 Stability test of sol

Stability of the nanocoatings on glass was determined with solar cells. The cases compared were blank, coatings with no catalyst, and coating with  $\text{NH}_4\text{OH}$  catalyst. In the comparison, voltages were recorded every day for one month during 11.00-15.00. Dust was intentionally sprinkled onto the glass surfaces every 7 days to assess self-cleaning, showing visible differences as in Figure 2.

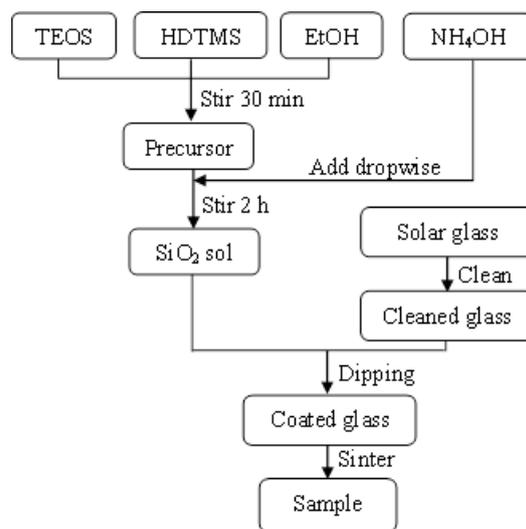


Figure 1. Procedure for making coated glass samples

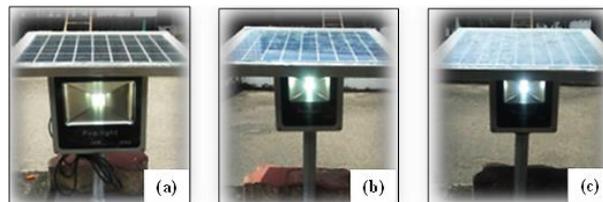


Figure 2. Assessing stability of the solar cell coatings. )a( Blank, )b( no catalyst, and )c( catalyst used.

### 3. Results and Discussion

#### 3.1 Effects of TEOS and HDTMS concentrations

The effects of TEOS concentration on the water-contact angle (WCA) of glass surfaces were assessed for fixed 1.0 vol.% HDTMS, as presented in Figure 3a. It is seen that the contact angle increased up to 115.41° for 6.0 vol.% TEOS in the sol. It was observed that in the sol-gel process TEOS is hydrolyzed and condensed to form a SiO<sub>2</sub> network, which is covalently bonded. The hydroxyl groups on the silica clusters are replaced by -Si-C<sub>16</sub> groups through oxygen bonds. The hydrophobicity of the sol-gel coatings is due to these long alkyl chains on the silica network, providing water resistance to the glass surface (Hussaina *et al.*, 2017).

The sol-gel coatings on glass surface with fixed TEOS loading at 6.0 vol.% while varying the concentration of HDTMS are presented in Figure 3b. The contact angle increased with HDTMS concentration. When the HDTMS concentration was rather low (less than 0.5%), the silica particles were randomly distributed without obvious aggregation, forming a thin coating on the glass surface. As HDTMS was increased from 0.5 to 1.5%, the silica particles started to aggregate to large clusters or lumps of various sizes, generating hierarchical micro/nano structures on the glass surface (Chang, Tu, Wang, & Liu, 2015). In this case, spherical water droplets were formed on the coated glass surface, displaying the high 117.39° contact angle.

#### 3.2 Effects of NH<sub>4</sub>OH catalyst on water-contact angle

The water-contact angle was mainly influenced by concentration of the NH<sub>4</sub>OH catalyst. Figure 4 shows the contact angles and images of the dip-coated films on glass surfaces. It can be clearly seen that the contact angle increased with NH<sub>4</sub>OH concentration. As the NH<sub>4</sub>OH content in treated sol increases from 0.05% to 1%, the water-contact angle on coating increases from 100.29° to 150.69°. Hydrophobicity is an important property of the sol-gel coating. With increasing hydrophobicity, the film stability can be significantly improved. Superhydrophobic surfaces possess high apparent contact angles, by definition exceeding 150°, which means the water droplet can easily roll off from the surface. Generally superhydrophobic surfaces exhibit roll-off angles less than 5 degrees, but very high quality superhydrophobic surfaces can exhibit roll-off angles of less than 1 degree (Simpson, Hunter, & Aytug, 2015). The case with 1.0% vol. NH<sub>4</sub>OH presented the highest 150.69° contact angle among the cases tested, and this case can be characterized as a superhydrophobic coating with a nanoscopic surface layer. This is because ammonia acts as a catalyst causing TEOS have dense silica particles and these increase the hardness of silica sol-gel particles as evidenced by threshold of laser induced damage (Shen & Li, 2011; Yuan, Yan, Huang, & Hong, 2016). As a result of the water-contact angle reaching superhydrophobic status, the surface will be highly water repellent with roll-off ability and self-cleaning properties.

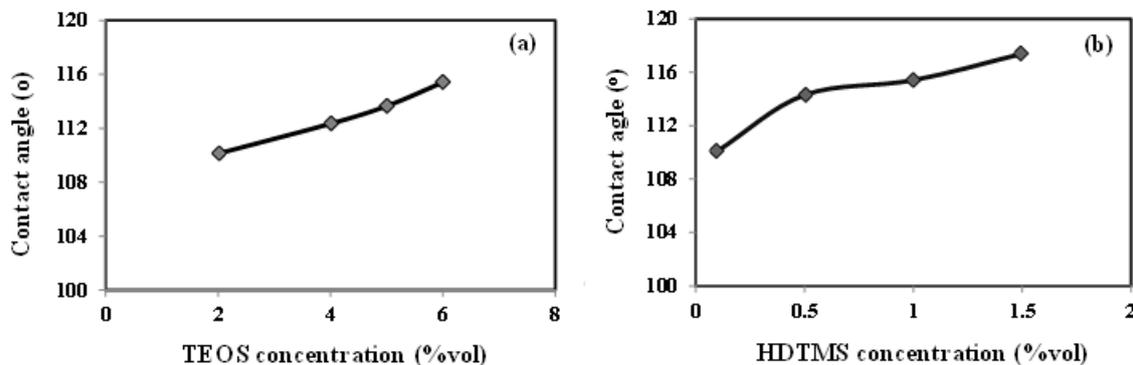


Figure 3. The water-contact angles tested by varying the concentration of )a( TEOS, and )b( HDTMS, on preparing the coating.

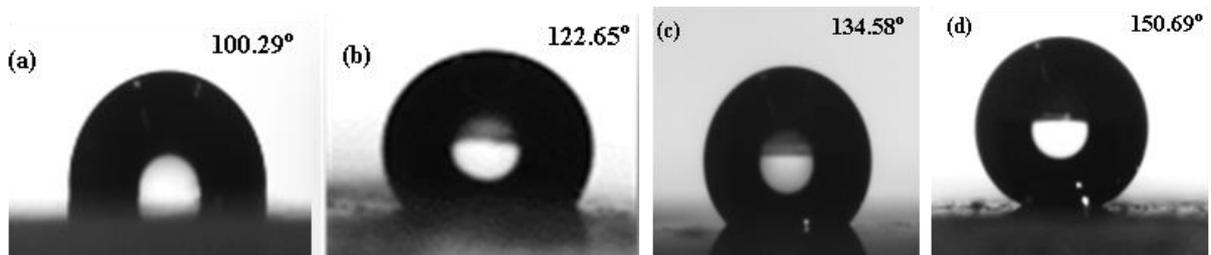


Figure 4. Photographs of water droplets with associated contact angles on the coated glass surfaces. )a( Treated with 0.05% NH<sub>4</sub>OH, )b( treated with 0.1% NH<sub>4</sub>OH, )c( treated with 0.5% NH<sub>4</sub>OH, and )d( treated with 1.0% NH<sub>4</sub>OH.

### 3.3 Effects of $\text{NH}_4\text{OH}$ catalyst on transmittance

The average optical transmittance was measured for 6.0% TEOS and 1.0% HDTMS case, and Figure 5 shows transmittances at 625 nm. The three cases compared were uncoated glass substrate (blank), sol-gel coating without catalyst, and treated with catalyst (1.0% vol.  $\text{NH}_4\text{OH}$ ). The 99.0% transmittance of glass substrate decreased to 97.5% on coating with sol-gel, while the sol treated with  $\text{Na}_4\text{OH}$  catalyst gave 94.3%. The results show that sol-gel treated with  $\text{Na}_4\text{OH}$  catalyst gave a slight decrease in light transmittance. However, the treated sol-gel still provided improved optical transmittance to a solar cell. The average transmittance reflects the stability of the coating. Therefore, the sol-gel coating possesses high transmittance, and anti-contamination properties simultaneously (Lin, Zheng, Yan, & Zhang, 2018). The results of SEM characterization showed that the layer thickness is in the range of 7 to 19  $\mu\text{m}$ .

### 3.4 Effects of nano coating on surface roughness

AFM topographical images of surfaces are presented in Figure 6. The roughnesses were 0.5909 nm Ra for the uncoated surface, 3.34 nm Ra for the coated surface B, and 0.2347  $\mu\text{m}$  Ra for coated surface C with catalyst, respectively. It can be noted that surface C is clearly much rougher than surface B. The advancing water-contact angle measured on surface C ( $150.69^\circ$ ) was larger than that measured on surface B ( $115.41^\circ$ ). These contact angles clearly indicate that increased surface roughness accompanied decreased wettability of the surface. According to the Cassie–Baxter model air trapped within micro scale particles reduces contact surface area between liquid drop and coating surface. The surface profiles showed that the sol-gel with catalyst  $\text{NH}_4\text{OH}$  surface C (had a uniform distribution of roughness). It was also found that the sol-gel with catalyst increased the roughness of the glass surface, which affects the droplet contact angle. The combination of self-assembling hydrophobic hexadecyl groups and rough surface of the sol-gel coating converted the glass surface from hydrophilic to superhydrophobic (Li, Xing, & Dai, 2008). When the catalyst in sol-gel reaches a critical level, the aggregates of silica particles in combination with the inherent microscale roughness of glass appear to create hierarchical micro/nano-structures on the glass substrate, causing superhydrophobicity (Chang *et al.*, 2015).

### 3.5 Effects on stability of sol

Time traces of voltages of solar cells with various coatings were recorded during outdoor exposure, and are seen in Figure 7. There were consistent changes in the voltages of solar cells with coatings by outdoors exposure for 30 days monitoring was already tested under aging with exposure to dust and degradation induced by sunlight irradiation. Uncoated solar cells and those coated with sol-gel without catalyst had gradual reductions in voltage by 40% and 20%, respectively. Over time, the solar cells coated with sol-gel with catalyst gave clearly higher voltages than uncoated solar cells, probably because the superhydrophobic surfaces were self-cleaning during rain or with morning dew, thus maintaining the performance in terms of voltage output from

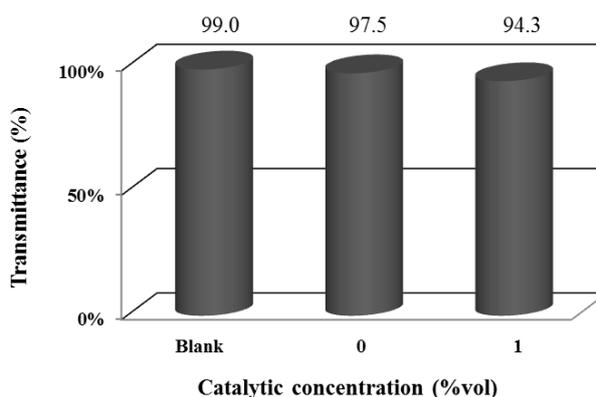


Figure 5. Effect of  $\text{NH}_4\text{OH}$  catalyst concentration on transmittance at 625 nm by UV/VIS Spectrophotometer.

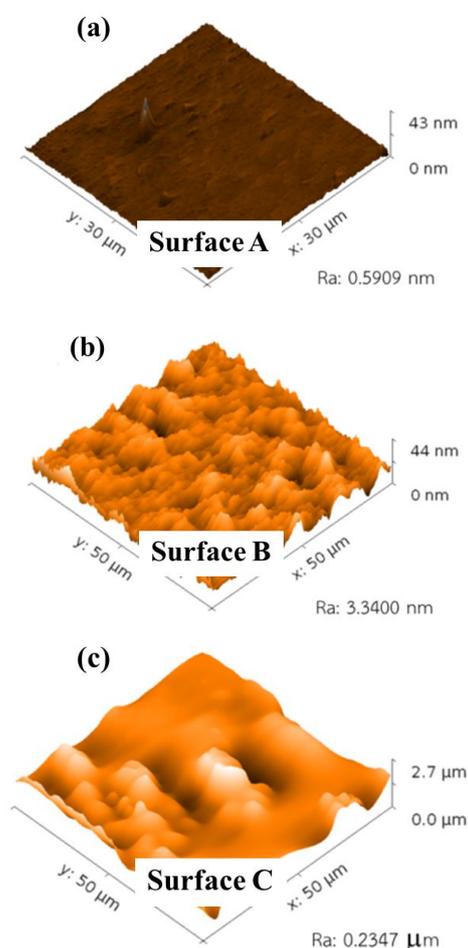


Figure 6. AFM surface topographical images of (a) uncoated glass substrate (surface A), (b) sol-gel coating without catalyst (surface B), and (c) coating treated with 1.0% vol.  $\text{NH}_4\text{OH}$  catalyst (surface C).

solar cell. The loss in voltage was less and is clearly seen different trend of voltage between coated and uncoated. The coatings should be stable over a long period, in order to warrant industrial production, and the 30-day test done is too

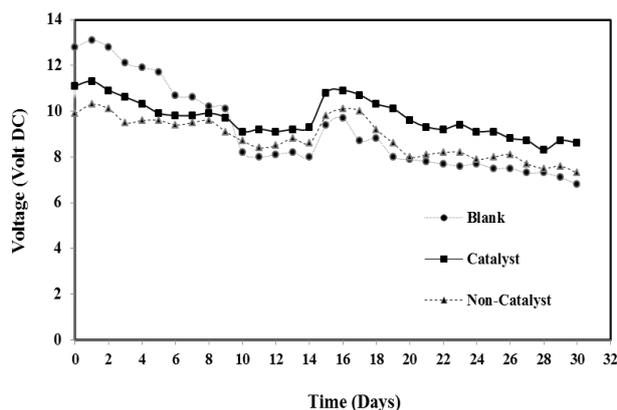


Figure 7. Time traces of solar cell voltage during outdoor exposure for up to 30 days of coated and uncoated solar cells.

short to assess this aspect. However, it clearly suggests that an inexpensive coating could help avoid cleanup/maintenance costs at solar panel installations. The dip-coating technique applied in this work provides high-performance specifications, simplicity of use and low costs.

#### 4. Conclusions

In summary, superhydrophobic surfaces were successfully prepared by sol-gel dip coating of glass substrates for solar cell covers. The thin film coating with optimum TEOS, HDTMS and  $\text{NH}_4\text{OH}$  contents of 6.0, 1.0, and 1.0 vol. %, respectively, had water contact angle indicating self-cleaning ability. The sol treated with  $\text{NH}_4\text{OH}$  catalyst proved to give the most advantageous coating, having the combination of high  $150.69^\circ$  water-contact angle with high transmittance. The superhydrophobicity achieved was facilitated by nanoscale roughness, imparted by aggregates of silica particles, and these coatings on glass surfaces exhibited good stability with outdoor exposure to the elements. The solar cells with coatings of sol-gel treated with  $\text{NH}_4\text{OH}$  catalyst had less loss of voltage than other cases with outdoor exposure, apparently due to their self-cleaning ability. The coatings demonstrated have potential for various outdoor applications. All commercial grade coating substrates for thin film deposition have low price.

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