Preparation and Characterization of Hydrophilic Silica Nanoparticle Coatings for Self-Cleaning Application

Parinda Bunchuaylue[1], Sakolpat Phalaruji[1], Nuengburut Laochokchai[1], Nataporn Sowasod[2*],
King Mongkut's University of Technology North Bangkok (Rayong Campus), Nong Lalok, Bankhai, Rayong 21120
Tanyakorn Muangnapoh[3]
National Science and Technology Development Agency, Klong 1, Klong Luang, Pathum Thani 12120
and Wiwut Tanthapanichakoon[4]
The Royal Society of Thailand, Sanam Sueapa, Dusit, Bangkok 10300

* *Corresponding Author: nataporn.s@eat.kmutnb.ac.th*
[1] *Undergraduate Student, Division of Chemical Process Engineering Technology, Faculty of Engineering and Technology.*
[2] *Assistant Professor, Division of Chemical Process Engineering Technology, Faculty of Engineering and Technology.*
[3] *Researcher, National Nanotechnology Center (NANOTEC).*
[4] *Fellow, Academy of Science. The Royal Society of Thailand*

Article Info

Article History:
Received: November 20, 2018
Revised: August 8, 2019
Accepted: September 13, 2019

Keywords:
Self-cleaning / Hydrophilic / 32 Silica Nanoparticles / Coating

Abstract

Self-cleaning coatings are of immense importance for certain technological applications. Such coatings may be classified into two major categories, i.e., superhydrophobic and superhydrophilic coatings. The objective of the present work was to investigate the formulation and characterization of self-cleaning superhydrophilic coatings for solar cell panels. The study aimed to formulate and characterize waterborne inorganic coatings of hydrophilic silica nanoparticles (SNP) enhanced with anhydrous sodium di-hydrogen phosphate (ASDP) and boric acid (BA) under various formulations in order to come up with the most suitable candidate. The coating thickness was measured with a nano search microscope, while the surface microstructure was characterized by scanning electron Microscopy. The water contact angle (WCA) was measured by a contact angle meter. A total number of 10 formulations for separate use in both simple painting and spraying methods were investigated; film thicknesses obtained from both coating methods were measured and compared to screen for the more promising coating method. WCAs of all 10 spray-coated formulations were measured and compared to come up with the most suitable formulation. Optimum weight ratio of SNP:ASDP:BA was noted to be 4:1:6 with average film thickness and contact angle of 2.0 μm and 13.0°, respectively.

การเตรียมและการตรวจสอบสมบัติของผิวเคลือบอนุภาคนาโนซิลิกาแบบชอบน้ำเพื่อประยุกต์ใช้เป็นสารเคลือบทำความสะอาดตัวเอง

ปริญดา บุญช่วยเหลือ[1] สกลพัฒน์ ผลารุจิ[1] หนึ่งบุรุษ เหล่าโชคชัย[1] ณฐพร โสวสด[2*]
มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าพระนครเหนือ วิทยาเขตระยอง ต.หนองละลอก อ.บ้านค่าย จ.ระยอง 21120
ธันยกร เมืองนาโพธิ์[3]
อุทยานวิทยาศาสตร์ประเทศไทย ต.คลองหนึ่ง อ.คลองหลวง จ.ปทุมธานี 12120
และ วิวัฒน์ ตัณฑะพานิชกุล[4]
ราชบัณฑิตยสภา สนามเสือป่า แขวงดุสิต เขตดุสิต กรุงเทพฯ 10300

** Corresponding Author: nataporn.s@eat.kmutnb.ac.th*
[1] นักศึกษาปริญญาตรี สาขาวิชาเทคโนโลยีวิศวกรรมกระบวนการเคมี คณะวิศวกรรมศาสตร์และเทคโนโลยี
[2] ผู้ช่วยศาสตราจารย์ สาขาวิชาเทคโนโลยีวิศวกรรมกระบวนการเคมี คณะวิศวกรรมศาสตร์และเทคโนโลยี
[3] นักวิจัย ศูนย์นาโนเทคโนโลยีแห่งชาติ
[4] ราชบัณฑิต สำนักวิทยาศาสตร์ ราชบัณฑิตยสภา

ข้อมูลบทความ

ประวัติบทความ :
รับเพื่อพิจารณา : 20 พฤศจิกายน 2561
แก้ไข : 8 สิงหาคม 2562
ตอบรับ : 13 กันยายน 2562

คำสำคัญ :
ทำความสะอาดตัวเอง / ไฮโดรฟิลิก / อนุภาคนาโนซิลิกา / การเคลือบ

บทคัดย่อ

เคลือบผิวที่ทำความสะอาดตัวเองได้มีความสำคัญยิ่งสำหรับการใช้งานเชิงเทคโนโลยีบางอย่าง เคลือบผิวดังกล่าวอาจแบ่งได้เป็นสองประเภทหลัก ได้แก่ เคลือบผิวเกลียดน้ำยวดยิ่ง (superhydrophobic) และเคลือบผิวชอบน้ำยวดยิ่ง (superhydrophilic) งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการกำหนดสูตรและสมบัติของสารเคลือบผิวชอบน้ำที่ทำความสะอาดตัวเองได้สำหรับแผงโซล่าร์เซลล์ โดยกำหนดสูตรและระบุสมบัติของเคลือบผิวชนิดสารอนินทรีย์ในน้ำ ซึ่งประกอบด้วยอนุภาคนาโนซิลิกาชอบน้ำ (SNP) ที่เสริมด้วยโซเดียมไดไฮโดรเจนฟอสเฟต (ASDP) และกรดบอริก (BA) ภายใต้สูตรต่างๆ เพื่อแสวงหาตัวแทนที่เหมาะสมที่สุด ทั้งนี้ วัดความหนาของผิวเคลือบด้วยกล้องจุลทรรศน์ชนิดนาโนเสิร์ช กำหนดลักษณะเฉพาะของโครงสร้างจุลภาคของพื้นผิวด้วยวิธีจุลทรรศน์อิเล็กตรอนแบบส่องกราด และวัดมุมสัมผัสน้ำ (WCA) โดยเครื่องวัดมุมสัมผัส เตรียมและตรวจสอบผิวเคลือบจำนวน 10 สูตรโดยเตรียมแยกต่างหากทั้งด้วยวิธีการทาสีอย่างง่ายและวิธีการฉีดพ่น และวัดความหนาของฟิล์มเคลือบที่ได้จากวิธีเคลือบทั้งสองวิธีเพื่อคัดหาวิธีที่มีแนวโน้มดีกว่า จากนั้นจึงวัดและเปรียบเทียบ WCAs ของฟิล์มเคลือบด้วยวิธีการฉีดพ่นทั้ง 10 สูตรเพื่อหาสูตรที่เหมาะสมที่สุด พบว่า อัตราส่วนน้ำหนักที่เหมาะสมของ SNP: ASDP: BA คือ 4: 1: 6 โดยมีความหนาเฉลี่ยของฟิล์มและมุมสัมผัสที่ 2.0 ไมครอนและ 13 องศา ตามลำดับ

1. Introduction

During the past decades, nanotechnology has attracted much attention among researchers and industries due to its high potential of adding significant values to the original materials. Thin film coating with nanomaterial can provide new properties and enhance performances of pristine surfaces for certain applications. This research was focused on the development of superhydrophilic self-cleaning coatings of solar panels with colloidal silica nanoparticles. A solar panel consists of a multitude of solar cells designed to efficiently convert solar energy into DC electricity but a major problem in the operation of solar cells is the need for frequent cleaning of their transparent protective glass layer. After installing and using solar panels for some time, fouling occurs on the glass layer through contaminated rain droplets, dust, stain, smoke, pollens and so on. The overall efficiency of solar transmission and absorption is thereby reduced. Therefore, coating of superhydrophilic silica nanoparticles on the solar panels to provide self-cleaning effect will eliminate the need for frequent cleaning while improving the long-term efficiency [1, 2].

Self-cleaning coatings may be classified into two major categories: superhydrophobic and superhydrophilic [3]. The objective of this research was to develop superhydrophilic self-cleaning coatings for solar panels which consist of colloidal silica nanoparticles with an average size of 30 nm, sodium di-hydrogen phosphate and boric acid in various formulations. The coatings can be applied by simple painting or fine spraying. To save cost of material, the ideal coating should have a minimum but sufficient thickness while displaying super-hydrophilicity and durability. The thickness of the hydrophilic nanosilica coating can be measured with a Nano Search Microscope (a combination of AFM and optical microscope). The microstructure of the nanoparticles in the coating can be characterized with Scanning Electron Microscopy (SEM). The degree of hydrophilicity of the coating was represented by the water contact angle (WCA) measurement using a contact angle meter. In this investigation, optical microscope glass slides, which have excellent transparency, were used for developing and testing the various formulations instead of actual glass layers used in solar panels. The present goal was to come up with an optimum coating material formulation that would give a minimum thickness while displaying superhydrophilicity. The durability and long-term characteristics of the resulting coating will be investigated and reported in the near future.

2. Materials and methods

2.1 Materials

Colloidal silica nanoparticles 3 %wt in isopropyl alcohol (IPA) were synthesized at NANOTEC using the Stöber process (30-50 nm). Boric acid was purchased from ACROS, USA. Anhydrous sodium di-hydrogen phosphate was purchased from QRëC, New Zealand.

2.2 Methods

Preparation of superhydrophilic coating solution from the above-mentioned 3 ingredients

In the case of formulation no. 1 in Table 1, 1 g of anhydrous sodium dihydrogen phosphate (ASDP) as binding agent and 1 g of boric acid for pH adjustment were put into a stainless-steel heating container, mixed with 50 ml of deionized water, and then heated while stirring. After the heated mixture achieved complete dissolution, it became transparent and colorless. Its weight was measured and the evaporated water was compensated to gain the desired additive compound. Next 4 g of silica nanoparticles 3 %wt in IPA was added to the additive compound and sufficiently stirred at room temperature to gain an inorganic waterborne coating solution having a final pH of preferably 6 to 7.

Table 1 Composition of formulations 1-10

Formulation (no.)	Silica nanoparticles 3 %wt in IPA (g)	Boric acid (g)	Sodium dihydrogen phosphate (g)	pH
1	4	1	1	5
2	4	3	1	4
3	4	6	1	4
4	4	12	1	4
5	4	1	3	5
6	4	1	6	5
7	4	1	12	5
8	8	1	1	6
9	16	1	1	6
10	32	1	1	6

Substrate for thin film coating

Microscope glass slides were used for thin film coating by fine spraying and simple painting methods.

Characterization of microstructure, film thickness and water contact angle.

The microstructure of the thin film of hydrophilic nanoparticles was observed through scanning electron microscopy (SEM) (Model SU8230, Hitachi, Japan).

The film thickness and surface condition was characterized with a Nano Search Microscope (Model OLS4500, Shimadzu, Japan). The static contact angle between a water droplet and the film surface was measured with a Contact Angle Meter (Model TC/TPC150, Dataphysics Instruments GmbH, Germany). At least 3 independent measurements were conducted for each thin film sample. The average contact angle and its standard deviation of each sample were reported in Table 2. [Wiwut: insert standard deviations in the Table; different codes (a) and (b) should be used for painted and sprayed film, respectively]

3. Results and discussion

Figure 1 shows photos of the coating solutions of formulations no. 1-10. It was found that numbers 1-7 were slightly opaque white and numbers 8-10 were slightly clear white and their pH values were found to range from 5 to 6. Katsumi Kishimoto [4] reported that coating solutions of silica nanoparticles with hydrophilic property should have a pH of 6-7 for solar panels. If the pH is too low, it can lead to corrosion of the panels.

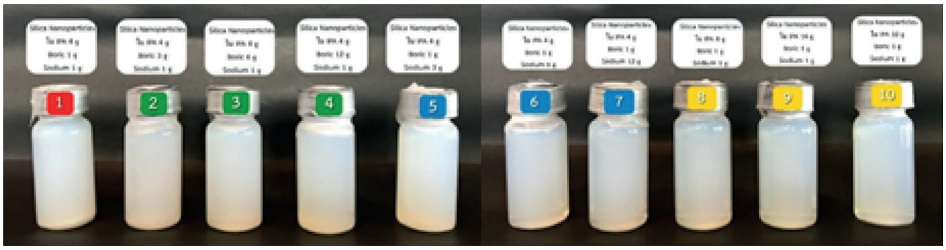

Figure 1 Coating solutions of formulations no. 1-10

For comparison, the coating solutions shown in Figure 1 were either sprayed or painted on microscope slides, which after natural drying resulted in the corresponding hydrophilic thin films. Their thicknesses were measured and summarized in Table 2.

3.1 Results from thin-film thickness analyzer (Nano Search Microscope)

Table 2 Comparison of average thicknesses of the hydrophilic thin films between (a) spraying and (b) painting methods, respectively

No.	Average thickness and std. dev. of painted film (a) (μm)	Average thickness and std. dev. of sprayed film (b) (μm)
1	2.3	3.1
2	0.2	7.1
3	0.2	6.2
4	6.1	0.2
5	1.2	5.1
6	4.1	0.2
7	5.1	7.2
8	3.1	6.0
9	3.1	2.1
10	4.1	5.0

Table 2 showed that 6 of the 10 sprayed coating had less thickness than their painted counterparts. It can be expected that with sufficient skill the former should have less thickness than the latter. Therefore, the spraying method is superior in terms of material cost saving; in addition a thinner film should have the same or more beneficial effect on solar cell efficiency if its durability turns out to be acceptable. Among the selected sprayed coatings, formulations no. 10, 8 and 9 were found to give the most, 2^{nd} and 3^{rd} thinnest films of 0.5, 0.6 and 1.2 μm, respectively. The key question is whether their higher degrees of hydrophilicity as represented by a smaller WCA lie in the same increasing order and are also among the smallest of all formulations.

3.2 Microstructure of thin films characterized by Scanning Electron Microscopy (SEM)

The microstructure of the thin films on the microscope slides was characterized with SEM. As examples, the micrographs of the painted surfaces of 4 formulations, namely, no. 1, 3, 6 and 9 were shown in Figure 2.

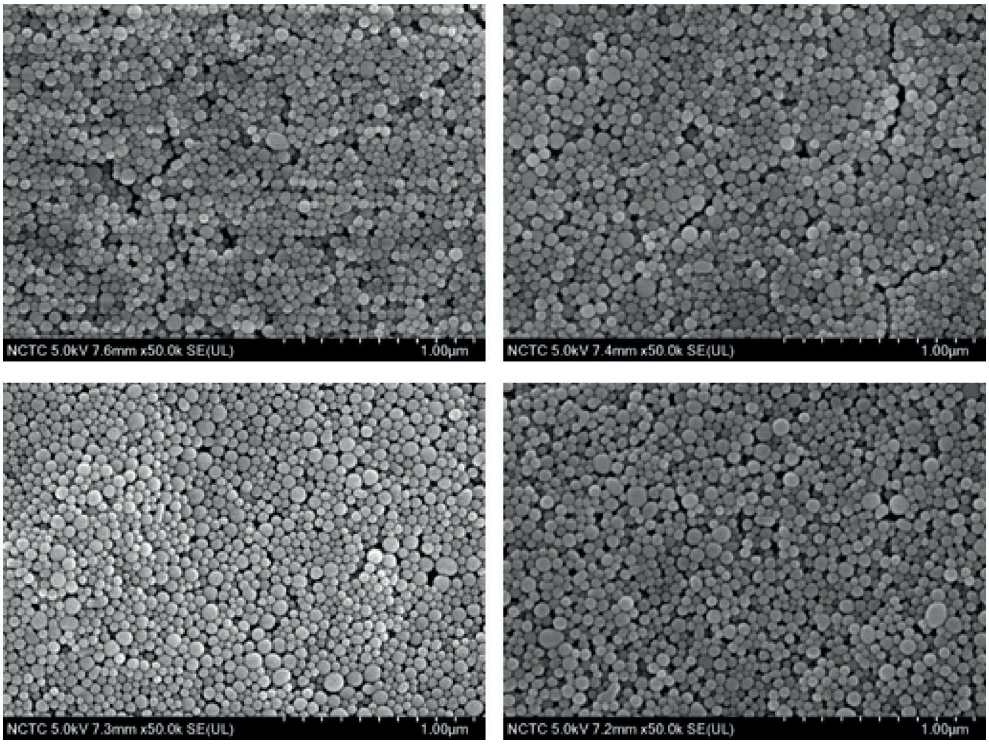

Figure 2 SEM micrographs of thin film surfaces (magnified 50,000 times): (A) Formulation No. 1, (B) No. 3, (C) No. 6, and (D) No. 9

In the Figure, it can be seen that the silica nanoparticles in different formulations were more or less similar in sizes and had a rather narrow size distribution with an average size of about 30 nm. The nanoparticles were densely and quite uniformly packed in formulations no. 6 and 9. In contrast, formulations no. 1 and 3 showed less uniform packing with sporadic holes and short vacant lines, especially no. 3 that tended to form relatively extended lines. It is logical to expect that a significant degree of non-uniform coating could have significant effect on the WCA and hydrophilicity. In any case, Figure 2 confirms that a number of the coating solutions could yield thin-film coatings of quite good quality.

3.3 Water contact angle on the thin film coatings

To investigate the hydrophilicity of the sprayed coatings, water contact angle was measured for each of the 10 formulations listed in Table 1 and summarized in Table 3. The photos of a water droplet lying on a blank slide (without coating) and the slide coated with formulation no. 9 are shown in Figure 3.

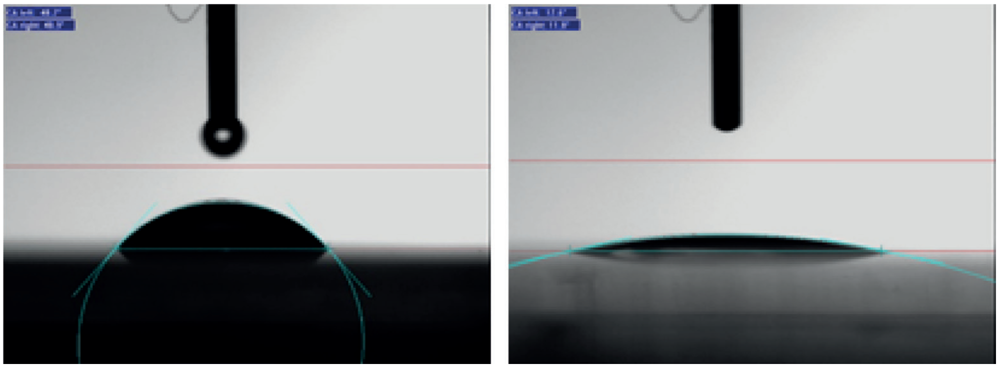

Figure 3 Contact angle test on (A) Blank slide, (B) Slide coated with formulation no. 9

From Table 3, the WCA on the blank slide was widest at 50.5°. The corresponding values for formulations no. 1, 3, 6 and 9, whose micrographs are shown in Figure 2, were found to be 25.5, 31.5, 13.0 and 12.7 degrees, respectively. It is not surprising that formulation no. 3 shows the poorest hydrophilicity (widest contact angle) among the four samples, which reflects the fact that it not only was less uniformly packed but also had numerous vacant sites without hydrophilic silica nanoparticles. Formulation no. 1 which had numerous small holes also showed rather poor hydrophilicity. This may be attributed to the fact the concentrations of nanosilica and/or binding agent in the coating solution of formulations no. 1 and 3 were among the lowest of the four. In addition, no. 3 had the thickest film of 2.6 μm and was most acidic with a lowest pH value of 4. As a result, the probability of non-uniform coating and undesirable vacant site formation was higher for formulations no. 1 and 3. When formulations no. 1 and 3 were compared, a much thicker film in the latter means that more water had to be evaporated at a lower pH since their nanosilica contents were the same.

Table 3 WCA of a water droplet on the thin films made by the spraying method

No.	Average contact angle (°)
0 (blank)	5.50 ± 2.8
1	5.25 ± 1.2
2	7.31 ± 0.7
3	5.31 ± 2.6
4	9.35 ± 0.3
5	7.19 ± 12.7
6	0.13 ± 3.0
7	7.19 ± 2.7
8	4.18 ± 6.5
9	7.12 ± 2.7
10	4.16 ±0.3

When formulation no. 6 was compared to no. 1, the former had a much smaller contact angle of 13.0° compared to 25.5° of the latter because of the beneficial effect of six times higher concentration of the ASDP binding agent. As a result the former had more uniform coating with less vacant sites. The highly beneficial effect of contact angle reduction by ASDP can be deduced when formulations no. 6 and 9 were compared. Their average contact angles of 13.0 ° and 12.7 ° were essentially the same, which fully qualified them as superhydrophilic thin film coatings with contact angles of less than 16.0° [3]. Apparently a 6 times higher ASDP concentration in the former managed to compensate the effect of 4 times higher nanosilica concentration in the latter while the sprayed film thickness of 2.0 μm of the former turned out to be significantly larger than the 1.2 μm of the latter.

It is common knowledge in the field of coating that the thickness of an excellent coating should be sufficiently thin but not too thin. If it is unnecessarily thick, the coated film will absorb more of the incidental solar energy and reduce the amount that can go through and reach the solar cells. However, if the film is too thin, a uniformly coated film with uniform thickness will be harder to achieve and the film may be less durable because it is easier to peel off. Since formulation no. 6 yielded a sufficiently thin film of 2.0 μm and the required amount of the costly nanosilica was only a quarter of formulation no. 9, formulations no. 6 and 9 should be selected for further investigation and verification for the coating of solar panels in terms of durability and long-term transmission characteristics.

4. Conclusions

Colloidal silica nanoparticles with narrow size distribution and average size of about 30 nm in isopropyl alcohol were synthesized for making coating solutions which displayed self-cleaning effect when coated on microscope glass slides. The investigated solution formulations consisted of silica nanoparticles, sodium di-hydrogen phosphate and boric acid at various weight ratios. The pH of the solutions was found to range from 5 to 6, which was sufficiently close to the recommended 6-7 [4]. Coating film thickness analysis confirmed that spray coating generally yielded thinner films than the corresponding paint coating. It was tentatively concluded that on the overall the optimum weight ratio of silica nanoparticles : sodium di-hydrogen phosphate : boric acid was the 4:1:6 of formulation no. 6. In this case, the average film thickness and water contact angle were 2.0 μm and 13.0°, respectively. The durability and long-term characteristics of the two selected coatings will be investigated and reported in the near future.

5. Acknowledgements

This research was supported by King Mongkut's University of Technology North Bangkok (KMUTNB-62-DRIVE-09). The authors are grateful to KMUTNB (Rayong Campus) and the National Nanotechnology Center (NANOTEC) for use of their lab facilities.

6. References

1. Jaesung, S., Shreya, K., Lalit, K.V., Mridul, S., Aaron, J.D., Charanjit, S.B. and Hyunsoo, Y., 2012, “A Practical Superhydrophilic Self-cleaning and Antireflective Surface for Outdoor Photovoltaic Applications,” *Solar Energy Materials and Solar Cells,* 98, pp. 46-51.

2. Hong, Z., Yang, H., Yuanhao, W. and Hongxing, Y., 2017, “TiO2/Silane Coupling Agent Composed Two Layers Structure: A Novel Stability Super-hydrophilic Self-cleaning Coating Applied in PV Panels,” *Energy*

Procedia, 105, pp. 1077-1083.

3. Xin, Y., Liqun, Z., Yichi, C., Baiqing, B., Jinlong, X. and Weiwei, Z., 2015, "Preparation and Characterization of Hydrophilic Silicon Dioxide Film on Acrylate Polyurethane Coatings with Self-cleaning Ability," *Applied Surface Science*, 349, pp. 916-923.

4. Kishimoto, K., 2012, Inorganic Waterborne Coating Agent and its Aqueous Solution, United State of America, US Patent 8,241,416 B2.