

Enhanced Solar Reflectance and Superhydrophobic Properties of Functionalized Silica-Coated Copper Phthalocyanine Pigments by the Sol–Gel Process

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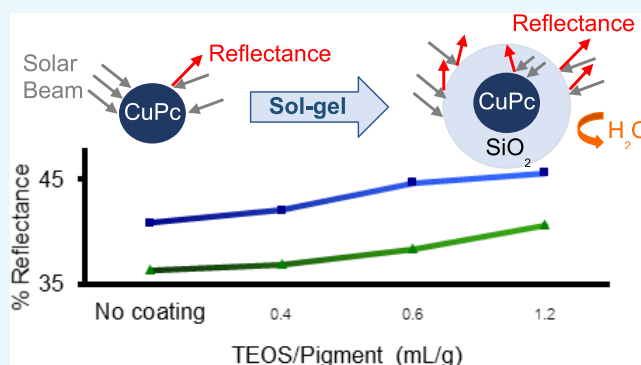
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ABSTRACT: This research studies the physical, superhydrophobic, and optical properties of functionalized silica-coated copper phthalocyanine (CuPc) pigments. The silica coating was confirmed by the size increase and the atomic ratio of silicon and copper of the coated pigments. Under optimal conditions, the green and blue shades of the pigments were enhanced as indicated by the increase in solar reflectance at 450–540 nm for the CuPc green and 380–520 nm for the CuPc blue. The total near-infrared (NIR) reflectance of the CuPc green and blue also increases by 10.6 and 11.5% compared to the uncoated pigments, respectively. The functionalized silica layer also adds a superhydrophobic property to the pigments. The contact angles of the functionalized pigments with water and oil are 154.4 and 54.3° for the CuPc green pigment and 142.9 and 78.1° for the CuPc blue pigment, respectively. The improved optical and hydrophobic properties make the pigment suitable for outdoor applications as an advanced protection layer to slow down material degradations from heat and humidity.



INTRODUCTION

Copper phthalocyanine (CuPc) pigments are widely used in inks, plastic, and cosmetics due to their brilliant green and blue colors, tinting strength, covering power, and resistance to acid and base.¹ Moreover, CuPc also has potential applications in organic solar cells^{2,3} and organic field-effect transistors.⁴

In tropical weather, outdoor furniture and buildings tend to suffer material degradations, including, cracks, rust, and fungi due to intense solar heat and high humidity. These problems increase maintenance costs and potentially damage the environment from waste disposal. Moreover, extensive absorption of sunlight through the exterior of buildings produces unwanted heat, which requires higher energy for air-conditioning to cool the buildings. The energy and resource consumption in buildings has enormous impacts on the environment, and this effect becomes more prominent as time passes due to an urbanization trend of the world.⁵

One of the methods to mitigate these problems is to improve the protective properties of pigments, including superhydrophobic and high near-infrared (NIR) reflective capabilities. A superhydrophobic coating can prevent the accumulation of dust, rust, and fungi due to its ability to repel water or the “lotus effect”. High-solar-energy-reflective pigments can also reduce thermal shock caused by a change in temperature⁶ and passively lower the indoor temperature when painted on a rooftop.⁷

However, pigments with these properties are relatively scarce, and the available commercial pigments with high NIR reflectance are usually bland. Thus, more vivid color pigments are needed.⁸

Silica coating on nanoparticles has been a focus in recent studies due to many applications, including magnetic particles in medical targeted delivery and treatments^{9–11} and sacrificial template for photonic structures.¹² The benefits of silica coating include high stability,¹³ nontoxicity,¹⁴ high specific surface area, improved reflective property,^{15–17} and low cost. For organic pigment systems, silica can be coated on the pigment to improve pigment dispersion in an aqueous system, the UV-shielding property, weatherability, and thermal stability.¹⁸

In this paper, functionalized silica coatings were applied to the CuPc pigments to improve their optical properties and superhydrophobicity. These capabilities can be characterized by studying the reflectance of the pigments in visible and NIR

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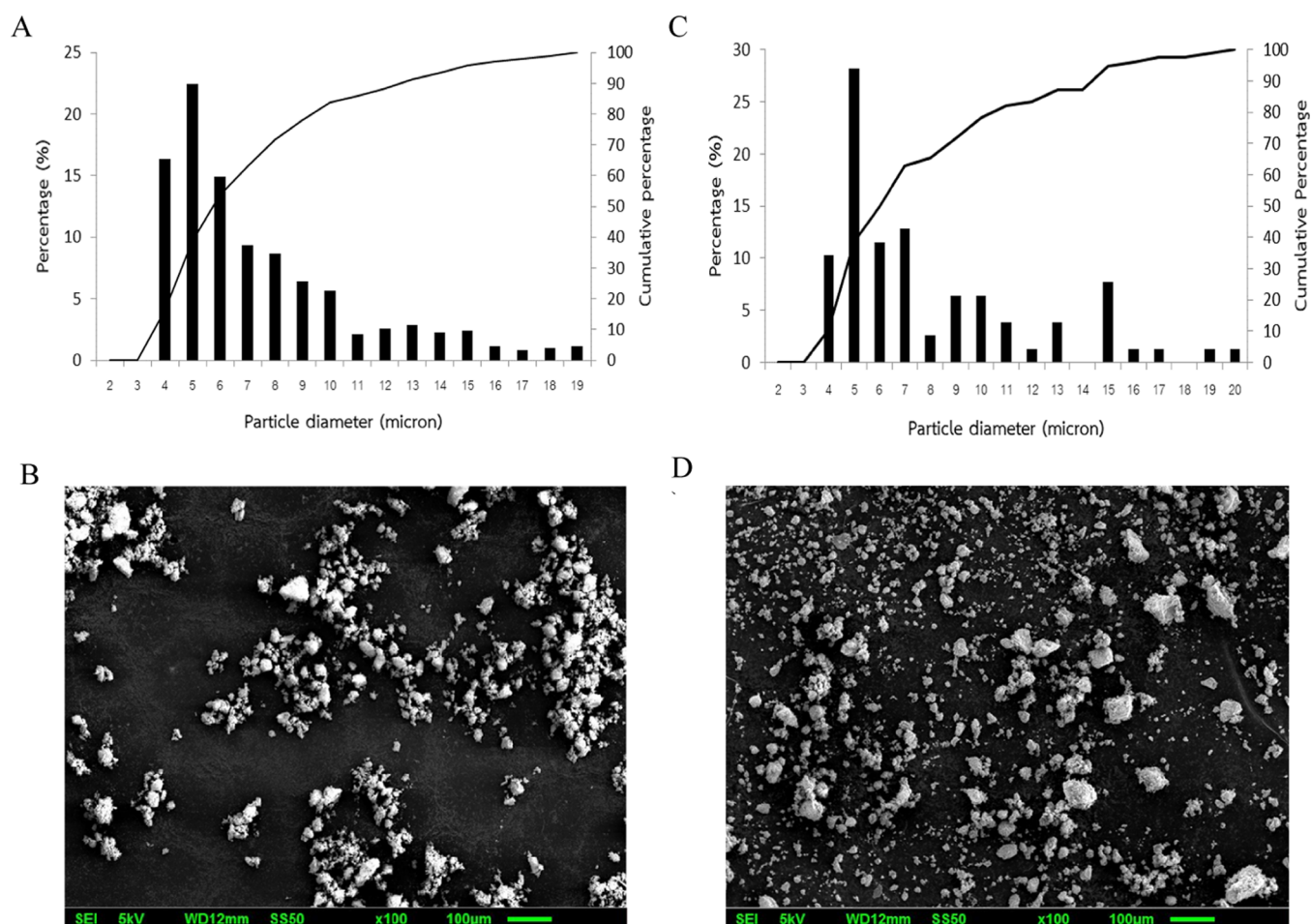


Figure 1. SEM images of the copper phthalocyanine pigments and their particle size distribution. (A, B) Particle size distribution and a SEM image of copper phthalocyanine green, respectively. (C, D) Particle size distribution and a SEM image of copper phthalocyanine blue, respectively.

wavelengths, as well as measuring their contact angles with water and oil. The sol–gel process was chosen due to its simplicity and effectiveness in modifying surface chemistry. Silica can be coated directly on the CuPc pigments without using a linker due to the formation of hydrogen bonds between the pigment and silica.¹⁹ Functionalization of fluoroalkylsilane on silica was conducted in the presence of an alkali-containing solution via hydrolysis and condensation reactions.²⁰

RESULTS AND DISCUSSION

Particle size distributions and scanning electron microscopy (SEM) images of the uncoated CuPc pigments are presented in Figure 1. Both pigments are polydispersed with most particle diameters ranging from 3 to 20 μm . Further, 80% of the particles have a diameter less than 10 μm .

A functionalized silica coating was applied to the CuPc pigments via a modified Stöber process. Surface morphologies of the functionalized CuPc were examined using SEM (Figure 2). The pigments were coated uniformly as shown in Figure 2B,D. Moreover, energy-dispersive X-ray (EDX) mapping confirmed the presence of silicon element in every particle, which suggests that silica is successfully coated on the CuPc pigments. Figure 3 presents the atomic ratios of silicon measured with wavelength-dispersive X-ray fluorescence (WDXRF) technique for each pigment at varied tetraethylorthosilicate (TEOS) concentrations. Figure 3A,B displays an increasing trend of silicon content proportional to the volume of TEOS increases. This can be

attributed to a higher ratio of silica present on the surface of the pigments. It is also noticeable that the CuPc blue samples display a higher average content of silicon compared to the CuPc green samples. This is probably due to the higher wettability of water on the CuPc blue pigments, which allows for more silica to be chemically deposited on the surface of the CuPc blue pigment. ImageJ analysis was performed on the SEM images to measure the size of the particle after silica functionalization. Table 1 shows a larger particle size for the pigment coated with a higher volume of TEOS. The results imply that the size of the pigments increases as more silica is coated on the CuPc pigment.⁵²

Figure 4A,B presents the reflectance of the CuPc green pigment with varied amounts of sol–gel precursors as a function of wavelength. Figure 4A depicts the solar reflectance of the CuPc green pigments between 380 and 700 nm. The reflectance of the pigments peaked at 500 nm, which is a characteristic of green/cyan color. The reflectance of the raw pigments is compared with that of the silica-coated pigment (1.2 mL/g). At wavelengths between 450 and 540 nm (blue-green), the reflectance of the coated samples exhibits 76.5–98.3% increases compared to the uncoated sample, enhancing the green color of the pigment.

For the pigment performance as a NIR-reflective pigment, the total solar energy reflectance between wavelengths 700 and 2500 nm is calculated by weighted normalization using solar energy distribution according to ASTM E903-12. As a result, the study found up to 10.4% increases in solar energy reflectance in the

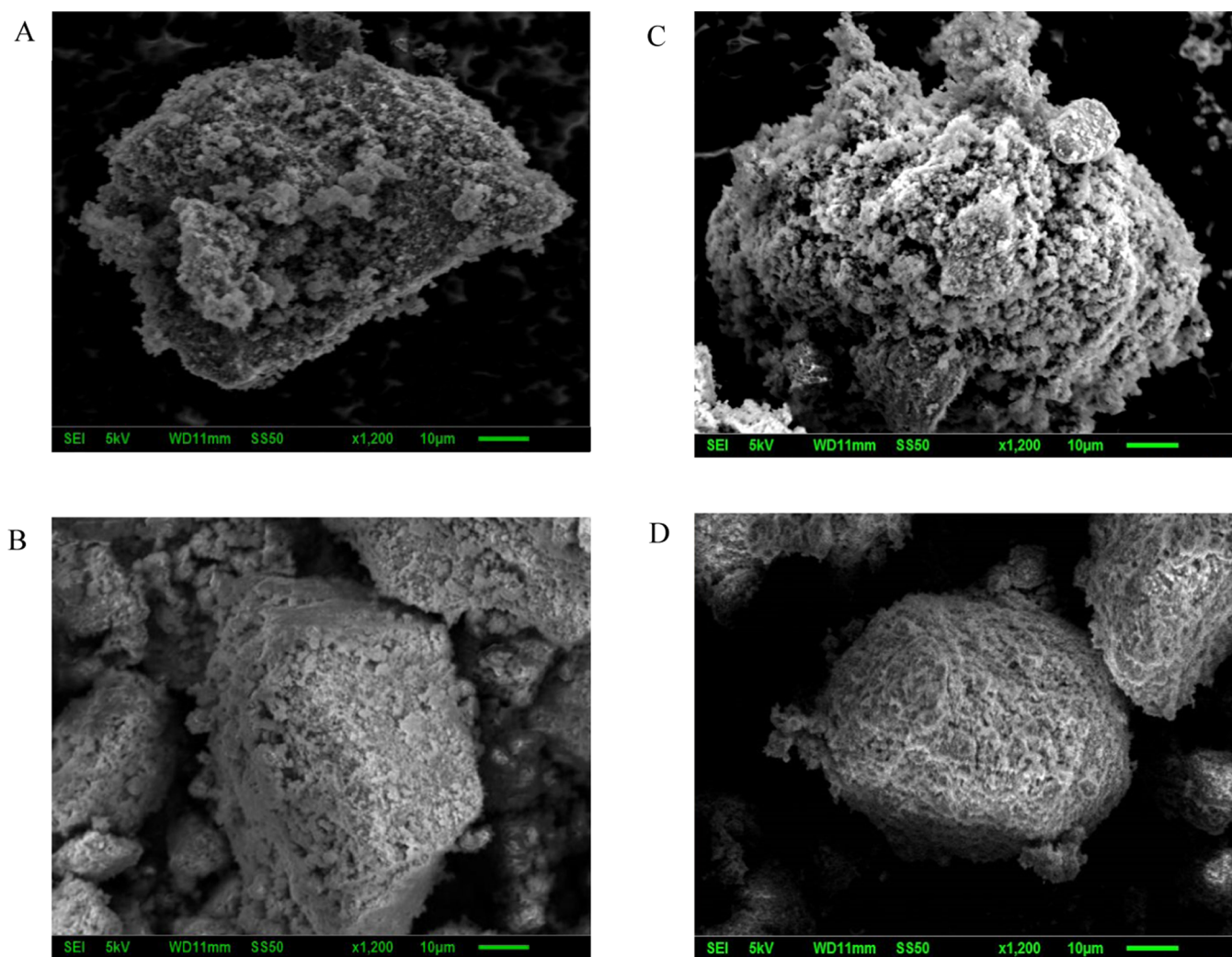


Figure 2. SEM images of the copper phthalocyanine pigments. (A) and (B) show CuPc green before and after the sol–gel process, respectively. (C) and (D) show CuPc blue before and after the sol–gel process, respectively.

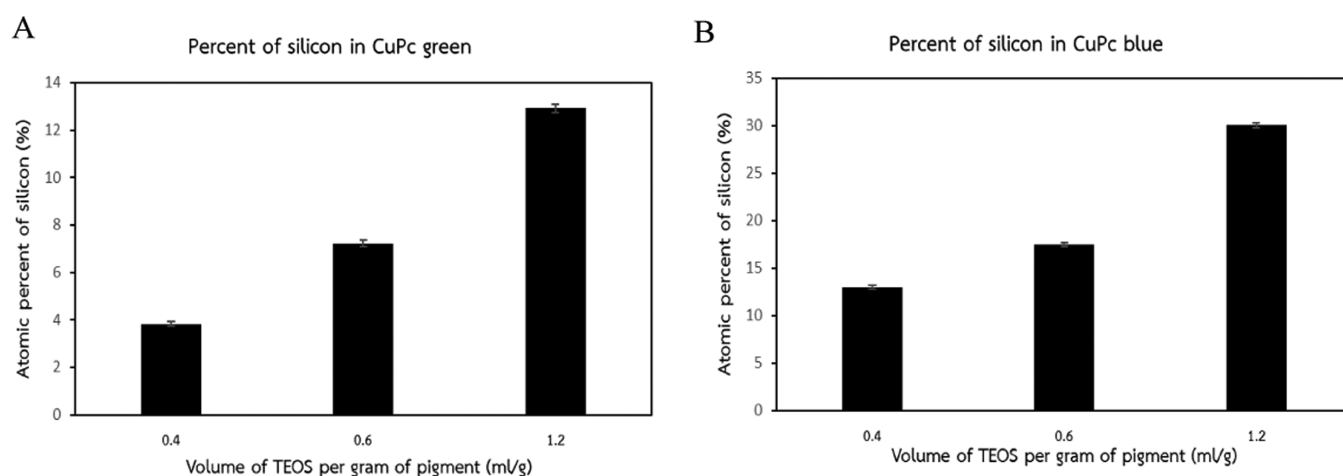


Figure 3. Atomic percent of silicon compared to copper as a function of the amount of TEOS. (A) CuPc green and (B) CuPc blue.

NIR region when compared to the uncoated sample as shown in Figure 4B.

Similarly, Figure 4C,D displays the reflectance of the CuPc blue pigment with varied amounts of sol–gel precursor as a function of wavelength. In Figure 4C, the reflectance peaks at

450 nm, which is a characteristic of blue color. In this case, the silica coating enhances the reflectance between 380 and 530 nm by 40.0–61.5% compared to the uncoated sample, while the reflectance increases slightly outside these wavelengths. For the NIR reflective property of the pigment shown in Figure 4D, the

Table 1. Average Diameter after Silica Coatings at Various Sol–Gel Precursor Concentrations^a

| Amount of TEOS/pigment (mL/g) | CuPc green (μm) | CuPc blue (μm) |
|-------------------------------|------------------------------|-----------------------------|
| no coating | 7.79 ± 3.48 | 8.47 ± 4.03 |
| 0.4 mL/g | 8.07 ± 3.85 | 9.90 ± 4.43 |
| 0.6 mL/g | 8.58 ± 3.93 | 10.48 ± 4.66 |
| 1.2 mL/g | 9.70 ± 4.30 | 10.49 ± 4.71 |

^aValues are measured from SEM images and analyzed using ImageJ.

silica-coated sample presents an 11.5% increase in NIR reflectance after coating.

It is worth noticing that while the silica-coated pigments enhance solar reflectance overall, the reflectance value for the coated sample at a wavelength longer than 1350 nm is reduced. For the visible spectrum, the silica coatings enhance the reflective wavelength between 450 and 540 nm for CuPc green and 380 and 520 nm for CuPc blue. This result suggests that the silica coating can be used to enhance the color shade of the pigment to be more vivid. For the NIR wavelength between 700 and 1300 nm, the pigment coated via the highest amount of TEOS in the study shows improved NIR reflectance with up to a 77% reflectance increase from the uncoated pigment at 820 nm. However, the reflectance of the uncoated pigment overtakes the coated sample at a wavelength higher than 1350 nm. The reason for this is that nanosilica has lower reflectance than the CuPc pigments at wavelengths 1200–2500 nm.

Tables 2 and 3 summarize the effects of silica coating on the colors and NIR reflectance of the pigments. The colors of the pigments were measured using a colorimeter according to the

Commission Internationale de l'éclairage (CIE) standard. The silica coatings brighten the pigments, and using a larger amount of TEOS yields brighter pigments as indicated by the larger L^* values. Moreover, the total NIR reflectance for the CuPc green pigment increases from the uncoated sample at 36.4 to 40.2% as the amount of TEOS increases. The CuPc blue pigments show a similar trend as the NIR reflectance increases from the uncoated sample at 40.9 to 45.2%.

Conley et al. performed computational and experimental studies on the effect of particle size and size distribution on NIR reflectance for the Si/SiO₂ system. They conclude that having a smaller average size can significantly enhance the NIR reflectance and narrower size distribution is not as important.²³ Therefore, it is possible to increase the NIR reflectance of the functionalized CuPc pigments using smaller particles on average without having homogeneous particles.

The contact angles of the functionalized pigments (TEOS/pigment 1.2 mL/g) with water and oil are shown in Table 4. The contact angles of the raw CuPc green and blue pigments with water are 113.3 and 71.6°, respectively. The contact angles of the pigment with oil could not be measured due to absorption of oil into the pigment films. After functionalization, the pigment films display an excellent hydrophobic property as indicated by high contact angles with water (>140°) and increased contact angles with oil, >70°. To improve the contact angle with water, it was suggested that a rougher surface of fluorinated silica increased the contact angle with water due to a large amount of air entrapped within the particles, which reduces the effective surface area between water and the particles.²⁴ This can be done using a larger fluorinated silica particle to create a thin film.^{25–27}

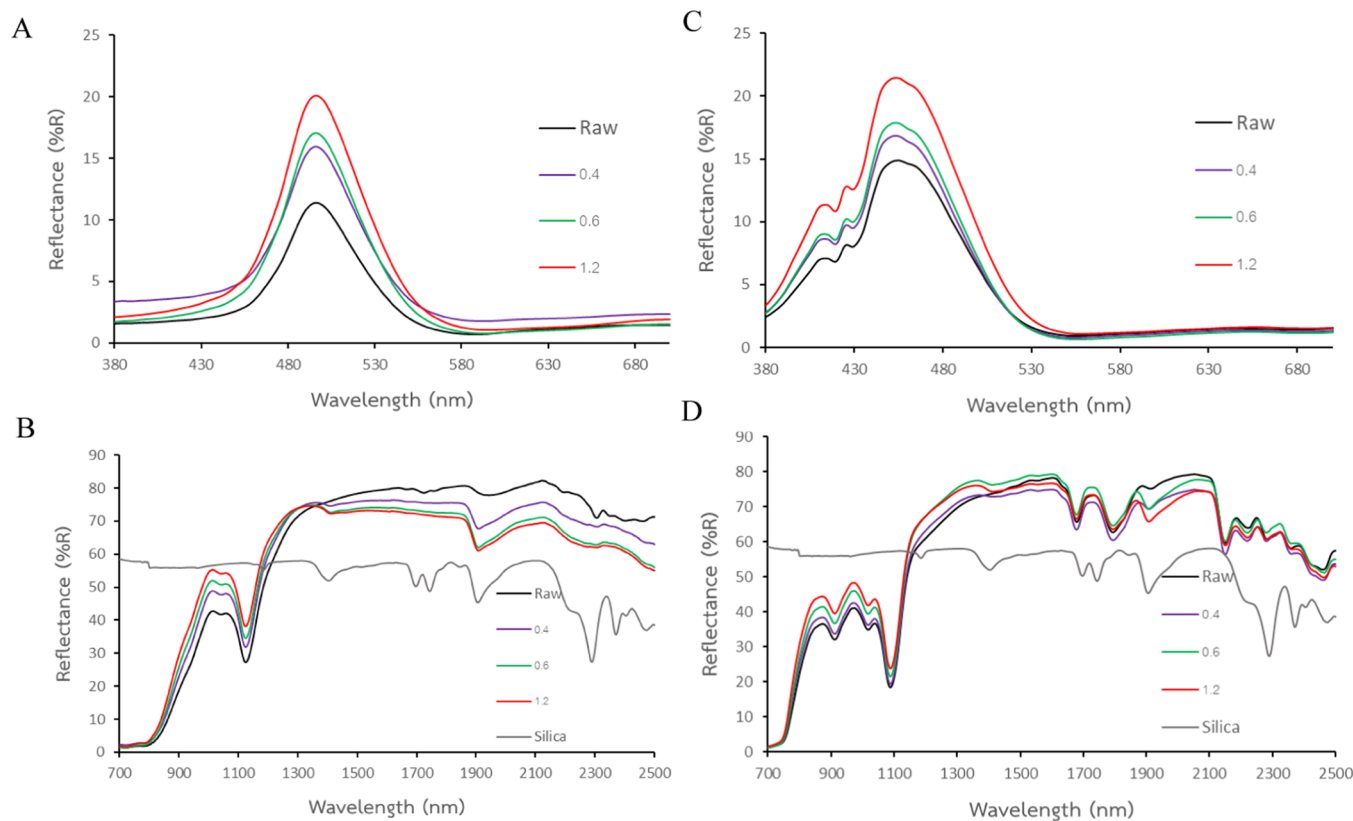


Figure 4. Solar reflectance spectrums of the silica-coated copper phthalocyanine pigments. Reflectance of CuPc green in the (A) visible wavelength (380–700 nm) and (B) near-infrared wavelength (700–2500 nm). Reflectance of CuPc blue in the (C) visible wavelength (380–700 nm) and (D) near-infrared wavelength (700–2500 nm).

Table 2. Color and NIR Reflectance for Silica-Coated Copper Phthalocyanine Green Pigments





| TEOS/Pigment (mL/g) | Color | L* | a* | b* | NIR Reflectance |
|---------------------|---|--------------|---------------|--------------|-----------------|
| No Coating |  | 19.78 | -37.82 | -1.70 | 36.4 |
| 0.4 |  | 25.36 ± 0.80 | -48.85 ± 0.77 | -1.20 ± 0.14 | 37.8 ± 1.1 |
| 0.6 |  | 30.02 ± 0.36 | -52.82 ± 0.59 | -1.29 ± 0.05 | 38.5 ± 0.8 |
| 1.2 |  | 33.62 ± 1.60 | -56.69 ± 1.27 | -1.09 ± 0.42 | 40.2 ± 0.9 |

Table 3. Color and NIR Reflectance for Silica-Coated Copper Phthalocyanine Blue Pigments





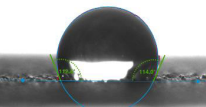

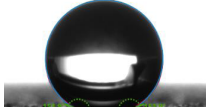
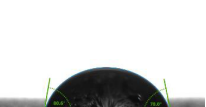
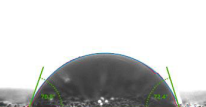



| TEOS/Pigment (mL/g) | Color | L* | a* | b* | NIR Reflectance |
|---------------------|---|--------------|--------------|---------------|-----------------|
| No Coating |  | 17.97 | 9.52 | -41.04 | 40.9 |
| 0.4 |  | 19.34 ± 0.72 | 11.31 ± 0.16 | -44.64 ± 0.87 | 42.3 ± 0.5 |
| 0.6 |  | 20.01 ± 0.30 | 11.24 ± 0.19 | -45.28 ± 0.37 | 44.3 ± 0.8 |
| 1.2 |  | 22.86 ± 0.15 | 8.5 ± 0.04 | -47.5 ± 0.22 | 45.2 ± 0.7 |

Table 4. Contact Angle of the Uncoated and Functionalized Pigments with Water and Oil

| | with water | with oil | with water | with oil |
|---------------------------|------------|----------|---|---|
| CuPc Green | 113.3 | N/A |  |  |
| Functionalized CuPc Green | 156.0 | 79.3 |  |  |
| CuPc Blue | 71.6 | N/A |  |  |
| Functionalized CuPc Blue | 141.1 | 74.6 |  |  |

In this study, size inhomogeneity most likely reduces the contact angle between the pigments with water because smaller particles can fill in the gap between larger particles, which increases the effective surface area between water and the pigments.

CONCLUSIONS

We have shown that the sol–gel silica coating technique can be applied to the CuPc pigments. SEM images showed that the sizes of most CuPc pigments ranged from 3 to 20 μm before the pigments were coated with fluoroalkylsilane-functionalized silica at various TEOS concentrations. After the coating process, the color of the CuPc pigments was brightened. The solar energy reflectance is enhanced 10.4 and 11.5% for green and blue CuPc, respectively, in the NIR region when compared to the uncoated sample. The pigment films show a strong hydrophobic property

with contact angles of more than 140°. These properties are attractive for a protection layer for outdoor applications.

Future studies of this research include a stability test in outdoor weather conditions to study the lifetime of the pigments and a detailed study on how size and size distribution affect solar reflectance and superhydrophobicity. Also, the contrast of contact angle with oil and water of the functionalized pigments suggests potential application as a membrane for water and oil separation.

METHOD

The blue and green CuPc pigments were provided by Thainakornpaint and Chemical Co., Ltd. The functionalized silica shells were coated on the CuPc pigments via a modified Stöber process.²¹ Silica coating and superhydrophobic functionalization were conducted in the same flask and solvent to reduce

production costs. In detail, the reaction medium comprised 1 g of copper pigment, 4 mL of deionized water, 12 mL of ammonia (25%, QR \ddot{C}), and 84 mL of absolute ethanol in a 100 mL round-bottom flask that was put under constant agitation to prevent particle coagulation. Then, varied amounts of tetraethylorthosilicate (TEOS) (98%, Sigma-Aldrich) were added to the medium, and the reaction was continued for 2 h, after which the reactants were heated to 60 °C and 1 mL of fluoroalkylsilane was added. The reaction was continued for 1 h, and the flask was left to cool naturally to room temperature afterward.

The samples were characterized using the following techniques: scanning electron microscopy and built-in energy-dispersive X-ray fluorescence spectrometry (7800F-JEOL). The SEM images were analyzed using a built-in function in ImageJ to calculate the particle size distributions. UV-vis-NIR spectrometry (Agilent) was performed in reflectance mode between 300 and 2500 nm. The WDXRF technique was used to measure the relative atomic concentration of silicon to copper. The total solar reflectance is calculated by weighted normalization using the solar energy distribution according to ASTM E903-12, "Standard Test Method for Solar absorbance, Reflectance and Transmittance of Materials Using Integrating Spheres", and with ASTM standard E891-87, "Beam normal (E891BN) for weights spectrometer measurements of near normal-hemispherical solar spectral reflectance". The colors of the pigments were measured using a colorimeter according to the Commission Internationale de l'éclairage (CIE) standard. To test the hydrophobic property, each pigment was spray-coated on 3 × 1 in. glass slides. Then, the contact angles between the pigment films and water/oil were measured (Mobile Surface Analyzer/Kruss Scientific).

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Notes

The authors declare no competing financial interest.

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