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Formulating 3-Chloropropyltriethoxysilane Modified Silica Nanoparticle Sprays as Hydrophobic Transparent Coatings onto Cotton Textiles

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Cotton textiles were transformed into hydrophobic fabrics *via* the application of 3-chloropropylthriethoxysilane-functionalized silica nanoparticle spray coatings. Silica particles were measured to be < 50 nm, as determined by dynamic light scattering (DLS). The incorporation of hexadecyltrimethylammonium bromide (HTAB), a surfactant, into the nanosilica alcohol-based sprays resulted in a suspension that was stable for at least a week. Stability and turbidity tests of samples point to smaller particle size (silica nanoparticles = 24.3 ± 8.5 nm) as the main contributor to possibly providing transparency, as evidenced when sprayed in colored (black) textiles, while still contributing to hydrophobicity/ superhydrophobicity of the cloth.

Keywords: hydrophobicity, silica nanoparticles, textiles

INTRODUCTION

In recent years, hydrophobic and superhydrophobic (Figure 1) surfaces have garnered interest because of their potential usage in anti-staining and antibacterial applications (Kamoun *et al.* 2017; Ali *et al.* 2019). The definition of hydrophobicity and superhydrophobicity has been popularly connected to contact angle measurements. In practice, a surface is considered hydrophobic if contact angle measurement is greater than 90 °. At this instance, no traces of residual water droplets can be observed (as it retracts cleanly) at this angle. When contact angle measurements become $\theta \geq 150$ ° (some literature prescribes $\theta \geq 145$ °), water adhesion to a surface is said to be zero and the surface is described to be superhydrophobic (Law 2014). This phenomenon – which is also observed in nature, particularly in the self-cleaning and water-repelling leaves of lotus plants – is aptly called the "lotus effect" (Marmur 2004; Lee and Michielsen 2006; Anjum *et al.* 2020). When water is spilled on a superhydrophobic surface, the liquid simply rolls off and picks up any foreign material with it, such as dirt and dust.

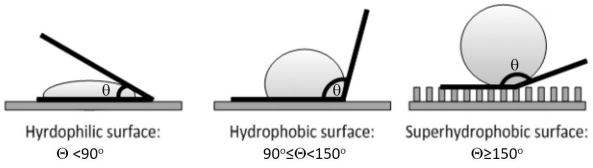

Figure 1. Hydrophilic, hydrophobic, and superhydrophobic surfaces.

The lotus effect on superhydrophobic/hydrophobic surfaces can somehow be described using either the Cassie-Baxter (Cassie and Baxter 1944) or the Wenzel (Wenzel 1936) models. Both models – which were derived from Young's equation, relating surface energy to contact angle measurements – assume uneven surface approximations. Whereas the Wenzel model describes the

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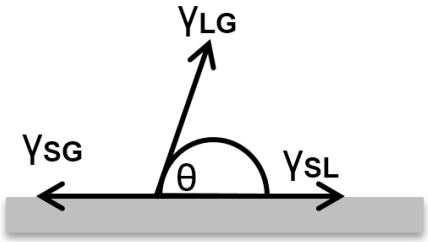
liquid to penetrate the groves of a homogeneous surface, the Cassie-Baxter approach refers to porous surfaces which should be more applicable to superhydrophobic/ hydrophobic sprays. In the Cassie-Baxter model, surfaces are assumed to have air pockets wherein water cannot penetrate through the nanofolds/ nanoparticles sprayed over surfaces. Hence, the water droplets are described to be resting upon asperities and attain the so-called Cassie-Baxter state.

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos\theta \quad (1)$$



Equation 1 (Young's equation) consists of θ as the contact angle, γ_{SG} as the solid-gas surface tension, γ_{SL} as the solid-liquid surface tension, and γ_{LG} as the liquid-gas surface tension.

Several methods of imparting hydrophobicity on surfaces exist: chemical vapor deposition, phase inversion, electrospinning, electrowetting, lithography, and etching (Berendjchi *et al.* 2011). For textiles, however, the solution-immersion method remains the simplest and most cost-effective approach of imparting water repellency, but this method produces a coating that has limited lifetimes due to wear and tear. Recently, the fabrication of superhydrophobic sprays had also become prominent and various brands had already released their own formulations in the market (Zhang *et al.* 2018; Tian *et al.* 2016). The use of sprays allows for on-demand application of hydrophobic coatings on various surfaces, hence its versatility. Nevertheless, most of these commercially-available water-repelling sprays all leave either a frosty white or visible film (Zhuang *et al.* 2017) on the surfaces, rendering it problematic for treating colored surfaces. They also require two coats, a base coat and a top coat, which takes overnight to dry.

In this study, we explored the formulation of hydrophobic sprays using 3-chloropropyltriethoxysilanes immobilized on silica particles as a suspension. The goal of this investigation was to come up with sprays that coat with adequate moisture repellency while still maintaining the aesthetics of the textile. We aim to do this by fabricating smaller (< 50 nm) particles. Silica – being inert, commonly available, relatively inexpensive (Caldona *et al.* 2019), and most of all, easy to modify and synthesize – was our nanoparticle of choice. While the use of long-chain silanes for silica functionalization seemed like a better choice, we utilized chloropropyltriethoxysilane as our hydrophobization agent because of its commercial availability and its potential for further derivatization.

MATERIALS AND METHODS

Chemicals and Reagents

3-chloropropyltriethoxysilane and HTAB were purchased from Gelest, Inc. and Sigma Aldrich Corporation, respectively. Tetraethyl orthosilicate (TEOS), ethanol, methanol, toluene, and ammonium hydroxide were purchased from Merck KGaA. All reagents were used as received. White and black cotton cloths (100% cotton) were procured.

Cotton Textile Scouring and Pre-treatment

Cotton textiles were cut up in square swatches (4 cm x 4 cm). Prior to any surface modification, the cotton swatches underwent scouring by being submerged in a mostly ethanol (> 80%) aqueous solution for 15 min. The swatches were then further dipped in toluene for another 30 min to remove the remaining impurities. After extraction, the swatches were dried in the oven for 2 h or until dry in preparation for subsequent spray coating.

Synthesis of Silica Nanoparticles for Spray Coatings

This method was adapted from the research work of Tadanaga *et al.* (2013) and Ogihara *et al.* (2015). Methanol, 25% ammonia, deionized water, and 1% (wt/v) HTAB were placed in a two-neck round bottom flask where ammonia served as a base catalyst. The reaction mixture was placed in a water bath, heated to 60 °C, and gently refluxed. TEOS was then added dropwise to the reaction and stirred further for up to 6 h. The reaction mixture was centrifuged thrice at 9000 rpm for 20 min each to let the agglomerated particles settle. These silica particles were then rinsed with ethanol, isolated, and oven-dried for 1 h at 60 °C. For control, surfactant was not added to one of the batches. This modification was done to properly analyze the effect of HTAB on minimizing agglomeration and decreasing particle size.

Functionalization of Silica Nanoparticles with 3-chloropropyltriethoxysilane

Synthesized silica nanoparticles (2.00 g) were placed in a two-neck round bottom flask with 40.0 mL of dehydrated toluene. This reaction mixture was sonicated then stirred at room temperature where 1.00 mL of

3-chloropropyltriethoxysilane was added dropwise. The mixture was then allowed to undergo reflux for up to 3 h. Similar to the collection of the silica nanoparticles, centrifugation was utilized and white powder samples obtained were isolated and oven-dried for 1 h at 60 °C.

Characterization of Silica Nanoparticles and Silane-functionalized Nanoparticles (Fabric Spray)

X-ray fluorescence (XRF, HORIBA XGT-7200 micro XRF analyzer) and Fourier transform infrared spectroscopies (FTIR, Shimadzu IR Affinity FTIR) were used to characterize the successful synthesis of the silica nanoparticles and silane functionalized nanoparticles. DLS (Malvern Zetasizer Nano ZS) was used to measure the nanoparticle size.

Suspension of Nanoparticles in Ethanol

The spray fabrication followed a previous study (Ogihara *et al.* 2015). Functionalized silica nanoparticles (0.10 g) were dispersed and added to 5.0 mL of ethanol. This mixture was stirred for 30 min. 10 µL of 1% (w/v) HTAB was added as a dispersant. One batch was left without the addition of surfactant for control to study the stability of the nanoparticles in spray over time.

Effectivity Study of Superhydrophobic/ Hydrophobic Spray

The transparency of the spray was characterized both quantitatively and qualitatively. Turbidity measurements of the suspensions were performed using an ultraviolet-visible integrating sphere spectrophotometer (UV-Vis IS, Shimadzu UV-2401PC). Qualitative analysis of the spray transparency was done by spraying onto black cotton textiles and subsequently observing any visible white film left on the substrate.

The water-repelling property imparted by the spray on treated surfaces was quantified through contact angle measurements of water droplets (10 µL) on white cotton textiles. The sprays deposited on the textiles were allowed to dry overnight before all qualitative analyses. For all test surfaces, three pumps of the spray treatment were deposited. The method was done using an improvised set-up employing a mobile phone (Macintosh Iphone7 plus pp) mounted on a level surface. Measurement was done using the DropSnake method processed under ImageJ software. The treated fabrics were also hand-washed before being subjected to a second contact angle measurement. This was done in order to account for the durability of the surface coating treatment.

RESULTS AND DISCUSSION

Preliminary Work

Prior to the current investigation, we used the solution-immersion method to try to immobilize 3-chloropropyltriethoxysilane functionalized silica particles (> 100 nm) onto cotton textiles. Our results showed that while this method provides adequate protection against moisture, its use was confined mostly to white-colored cloth (anti-staining studies, Figure 2) and the lifetime of its coating on textile was limited by wear and tear (SEM images, Figure 3). Because of this, we decided to explore the creation of silane-coated nano sprays based on the same materials used above. Formulating hydrophobic sprays should allow the interplay of hydrophobicity as imparted by the introduction of 3-chloropropyl triethoxysilane, whereas nano-sized roughness of the silica particles reinforces the lotus effect while maintaining the desired transparency of the coating. For this work, special care was undertaken to limit the size of the silica particles to < 50 nm.

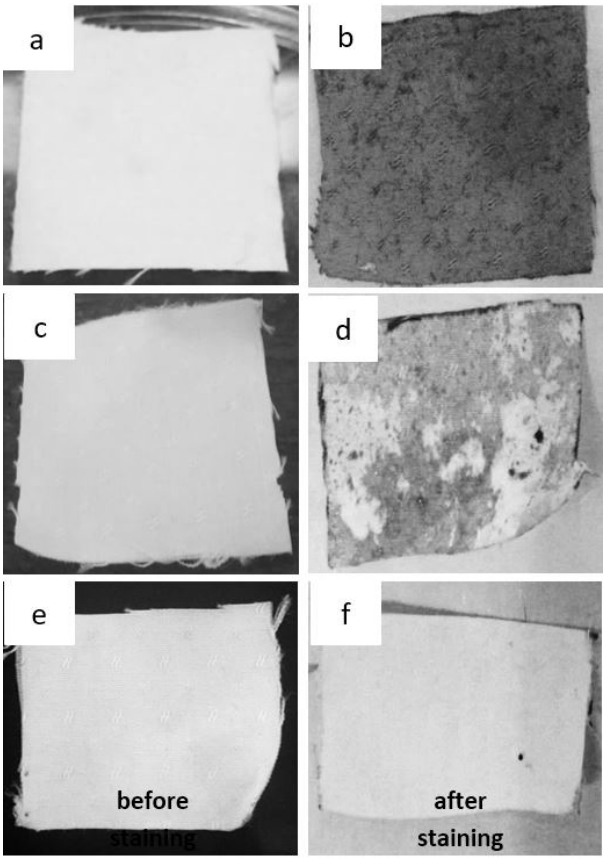


Figure 2. Blue food coloring staining treatments for untreated (a and b), 3-chloro propyltriethoxysilane-treated (c and d), and silica-functionalized treated cotton textiles (e and f).

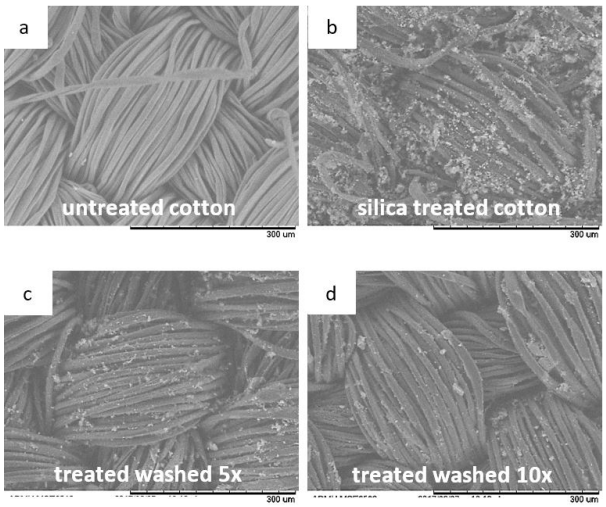


Figure 3. SEM images of untreated cotton *vs.* treated cotton (solution immersion method). Washing the treated cotton erodes the silica particles but still shows partial water repellency after 10 washing rounds.

Modified Silica Nanoparticles Synthesis and Characterization

The typical Stöber sol-gel reaction synthesizes particles ranging from 100–2000 nm in diameter. For the sprays to demonstrate hydrophobicity and even superhydrophobicity, the silica particles produced should introduce the necessary nano-textured roughness required to create a layer of air pockets acting as a physical barrier to liquids. Additionally, for this study, a much smaller diameter is needed in order to achieve the desired transparency. Specifically, a particle size of less than 50 nm was targeted. To ensure this, the reaction was performed at 60 °C. It was hypothesized that an increase in temperature should result in a high nucleation rate, which subsequently results in a smaller size. Because a lower dielectric constant (ε) favors particle growth as it minimizes the repulsive force between formed particles (Lenoble 2007), methanol – with a higher ε – was used as the solvent instead of ethanol (32.6 *vs.* 24.3). Furthermore, the TEOS concentration (affects SiO_2 formation and concentration), ammonia (pH change and stability of sol), and deionized water (resulting in higher SiO_2 concentration and larger particle size) all influence particle size and were, thus, varied (Tadanaga *et al.* 2013).

All experimental parameters for the preparation of silica nanoparticles are tabulated in Table 1.

The mean particle diameters of the synthesized silica nanoparticles were measured using DLS (see Appendix Figures I–III) while in suspension. The results are tabulated in Table 2.

The formulations for Samples 1 and 2, with a targeted particle size of 10 nm, were patterned after the study conducted by Tadanaga *et al.* (2013). While these results were favored, problems in the collection and isolation of the product for further modification were encountered for both samples. Extensive uses of the centrifuge and rotary evaporator were deemed ineffective. Hence, instead of directly synthesizing silica nanoparticles with extremely small particle size, it was opted to follow a formulation for silica with bigger particle size and subsequently work on reducing the diameter – if possible – from there.

A formulation for silica nanoparticles with a mean particle size of 50 nm was instead followed (Altin 2009). The DLS spectrum reports a mean particle size of 45.0 nm with a polydispersity index (PDI) of 0.355 (Sample 3). PDI is used to estimate the average uniformity in size of a particle in solution. For nanoparticles, larger PDI values correspond to a larger size distribution in the sample. Samples with PDI < 0.1 are considered monodisperse (Hughes 2015). This formulation resulted in an opaque white suspension and the synthesized silica nanoparticles were readily collected through centrifugation to obtain a white powder. To prevent particle agglomeration and easier re-suspension of particles, a quaternary ammonium surfactant (HTAB) was added to one batch of the same formulation. It was hypothesized that a surfactant lowers the surface tension at the interface between materials. The addition of surfactants modulates the available surface energy of the particles so that the surface tension decreases, thereby allowing more particles to escape the aggregation process (Singh *et al.* 2011).

The DLS spectrum of Sample 4 reported a mean particle size of 37.7 nm with a PDI of 0.455. This verifies the effectiveness of surfactant addition to particle size reduction. A final formulation, also reported by Altin (2009), was done (Sample 5) to yield a mean particle size

Table 1. Silica nanoparticle formulation using modified Stöber method. All reactions were performed at 60 °C for 24 h.

	TEOS (mL) (± 0.1)	**Ammonia (mL)** (± 0.1)	**DI[a] (mL)** (± 0.1)	**Methanol (mL)** (± 0.1)	**HTAB (µL)[b]** (± 1)
1	1.5	1.6	–	50	–
2	1.5	1.0	2.8	50	–
3	3.3	0.6	0.5	20	–
4	3.3	0.6	0.5	20	10
5	0.4	0.6	–	9.7	10

Table 2. Particle size of silica nanoparticles using DLS.

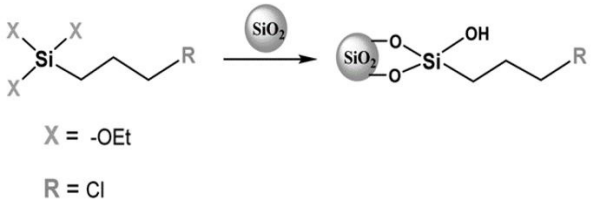
	Particle size (nm) (± SD)	PDI[a]
1	6.5 (± 1.6)	0.192
2	7.4 (± 1.9)	0.209
3	45.0 (± 8.1)	0.355
4	37.7 (± 7.9)	0.455
5	24.3 (± 8.5)	0.410

[a]Polydispersity index (PDI); smaller PDI narrower size distribution

of 24.3 nm. The surfactant (HTAB) was readily added to this reaction mixture. Ultimately, only Samples 3, 4, and 5 were successfully isolated and used in subsequent silane functionalization procedures.

Functionalization of Silica Nanoparticles with 3-chloropropyltriethoxysilane

The isolated silica nanoparticles were functionalized with 3-chloropropyltriethoxysilane to impart hydrophobicity (Scheme 1). In this reaction, the silane undergoes a condensation reaction with nanosilica surfaces, forming a covalent attachment with the removal of ethanol. We envisioned this functionalization procedure to correspond to the topcoat in commercially available formulations. Because silane is being directly immobilized on the silica surface, the two separate coats of the sprays in the market are effectively being combined into one. All three isolated silica samples underwent functionalization. A white powder was collected after centrifugation.



Scheme 1. Immobilization of silanes into silica particles.

he FTIR spectra (Figure 4) of the non-functionalized nanoparticles showed the characteristic Si-O-Si stretch at the 1000–1200 cm^{-1} region and Si-O-Si bend at the 400–500 cm^{-1} region.

The spectrum of the 3-chlorotriethoxysilane functionalized silica nanoparticles, however, showed a peak at the 2850–2950 cm^{-1} region. This corresponds to C-H stretching. Another peak is seen at the 600–800 cm^{-1} region, which in turn signifies C-Cl stretching. This signifies the successful immobilization/ covalent bonding of the chloropropyl-terminated silane onto the silica surface. These findings are further backed up by XRF data (see Appendix Table I), where a significant increase in the relative chlorine

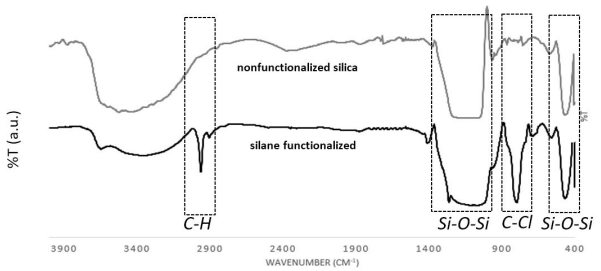


Figure 4. FTIR spectra of nonfunctionalized and functionalized silica nanoparticles.

content with respect to silicon was detected in the 3-chloropropyltriethoxysilane-coated samples.

Formulation and Stability of Spray Suspension

The silane-functionalized silica nanoparticles were then suspended in ethanol to create the sprays. HTAB was added to stabilize the suspension. Figure 5 showed the sprays with and without the addition of HTAB before and after a week of observation.

Figure 5. Spray suspensions at the start (a) and after a week (b) of observation. The silane-functionalized silica suspension was more stable with HTAB addition.

Both sprays exhibited opacity at the onset. However, after a week of observation, a clear solution with sedimentation was obtained for the suspension without any addition of HTAB, as evidenced by the appearance of the text placed behind the bottles. The suspension with HTAB, on the other hand, displayed little to no change in appearance. This proves the ability of the surfactant to disperse the nanoparticles.

Hydrophobicity/ Superhydrophobicity of Spray Coatings

All in all, three sprays with HTAB were successfully formulated. Spray A used Silica Sample 3 (45.0 nm), Spray B used Silica Sample 4 (37.7 nm), and Spray C used Silica Sample 5 (24.3 nm). The water-repelling property of the spray coatings was evaluated using the standard method reported by the American Association of Textile Chemists and Colorists (AATCC 2021). Figure 6 shows the contact angle measurements of cotton textiles treated with the sprays.

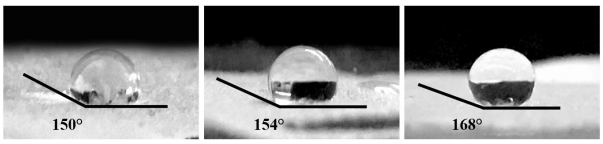


Figure 6. Contact angle measurements on cotton textile using (L–R) Sprays A, B, and C. Standard deviation, ± 2, ± 3, and ± 4 respectively (two trials).

An increasing contact angle is observed with decreasing particle size of 3-chloropropyltriethoxysilane-functionalized silica. This can be attributed to the presence of a finer layer of surface roughness, creating air pockets and greater surface area for the smaller particle size. As air and water adhere less compared to water and solids, respectively, these air pockets aid the suspension of the liquid – increasing its surface tension (Miwa 2000). In other words, the trapped air in the interstitial spaces of the roughened surface lessens the liquid-to-solid contact area.

Upon simple handwashing, a significant decrease in contact angle was observed for all spray coatings (Figure 7). Because the spray treatment was merely a physical one, this result is expected. It should be noted that for Sprays B and C, the contact angle after one washing is still well within the range of hydrophobicity.

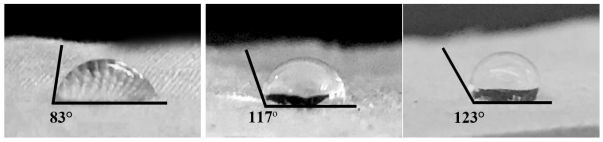


Figure 7. Contact angle measurements on cotton textile after 1x washing using (L–R) Sprays A, B, and C. Standard deviation, ± 1, ± 3, and ± 5 respectively (two trials).

Transparency of Spray Coatings

Turbidity measurements were undertaken to assess the transparency of the 3-chloropropyltriethoxysilane-functionalized nanosilica coatings on cotton cloth. Because turbidity describes the amount of light scattered or blocked by the suspended particles, these measurements evaluate the cloudiness or haziness of a fluid caused by the dispersed particles. Low turbidity indicates a clear sample, while high turbidity characterizes an opaque sample (Miwa 2000). In the UV-Vis IS measurement of turbidity, the % turbidity of a sample is given the formula:

$$\%\ turbidity = \frac{T - T_0}{100 - T_0} \times 100 \qquad (2)$$

Equation 2 (% turbidity) consists of T as the measured transmittance and T_0 as the transmittance for the turbidity zero point.

The % turbidity data of the sprays are summarized in Table 3. Results show that as particle size of the suspended silane-functionalized silica nanoparticles decrease, so does % turbidity of their corresponding sprays. We hypothesize that this is because the scattering of light is dependent on size parameters where larger particles would have multiple light-scattering centers. This directly influences the turbidity of the mixture, resulting in a hazier suspension. A smaller particle size, on the other hand, would have a smaller cross-section for scattering – resulting in a clearer suspension (Cheng 2010). Qualitatively, the transparency of the spray coating was evaluated by testing the treatment on colored fabric (Figure 8).

Table 3. Turbidity data of sprays (UV-Vis IS).

Spray	Particle size (nm)	% turbidity
A	45.0	77.1
B	37.7	49.2
C	24.3	34.8

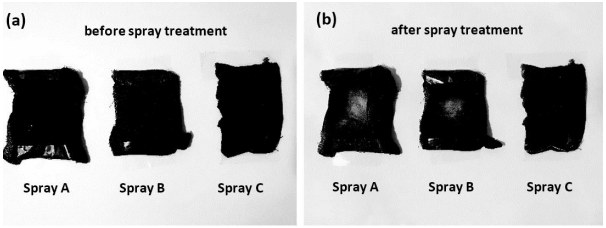


Figure 8. Dark-colored fabrics before (a) and after (b) spray treatment.

It is evident that a white film is present in the treated samples because of the nanoparticles. A larger area of the white film is present in the fabric treated with Spray A compared to the fabric treated with Spray B. This indicates a more opaque mixture for Spray A, which agrees with the quantitative data. It can also be observed that a near-colorless coating from Spray C was deposited on the fabric. This further corroborates the relationship between particle size and transparency.

CONCLUSION

In conclusion, hydrophilic cotton textiles were successfully transformed to hydrophobic fabrics using either silica surface immobilization or with the use of a silica nanoparticle spray. Both methods made use of 3-chloropropyltriethoxysilane as the hydrophobic coating agent. While silica-surface immobilization experiments demonstrate adequate water repellency, its limited use

warranted us to explore and fabricate silane-coated nanosprays. The sprays proved to be superhydrophobic achieving transparency and stability with smaller size particles and the addition of surfactants. Efforts are now underway to extensively investigate and improve the stability of these colloidal sprays.

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NOTES ON APPENDICES

The complete appendices section of the study is accessible at http://philjournsci.dost.gov.ph

REFERENCES

[AATCC] American Association of Textile Chemists and Colorists. 2021. Manual of International Test Methods and Procedures. Research Triangle, NC.

ALI S W, SHAHADAT M, SULTANA P, AHAMMAD SZ. 2019. Advanced Textiles for Wound Care, 2nd Ed. Woodhead Publishing Elsevier. p. 489–508.

ALTIN B. 2009. Synthesis and Characterization of Monodisperse Silica Based Functional Nanoparticles for Multi-Purpose Applications [MS thesis]. Izmir Institute of Technology. p. 1–97.

ANJUM AS, ALI M, SUM KC, RIAZ R, JEONG SH. 2020. Self-assembled nanomanipulation of silica nanoparticles enable mechanochemically robust super hydrophobic and oleophilic textile. J Colloid Interf Sci 563: 62–73.

BERENDJCHI A, KHAJAVI R, YAZDANSHENAS M. 2011. Fabrication of superhydrophobic and antibacterial surface on cotton fabric by doped silica- based sols with nanoparticles of copper, Nanoscale Research Letters 6: 594.

CALDONA EB, SIBAEN JW, TACTAY CB, MENDIOLA SLD, ABANCE CB, ANES MP, SERRANO FDD, DE GUZMAN MMS. 2019. Preparation of spray-coated surfaces from green-formulated superhydrophobic coatings. SN App Sci 1(12): 1657.

CASSIE ABD, BAXTER S. 1944. Wettability of Porous Surfaces. Transaction of the Faraday Society 40: 546–561.

CHENG WP, CHEN WY, YU RF, HSIEH YJ. 2010. The Relationship Between Particle Size and Turbidity Fluctuations in Coagulation Process. Journal of Residuals Science and Technology 7(2): 87–94.

HUGHES JM, BUDD PM, GRIEVE A, DUTTA P, TIEDE K, LEWIS J. 2015. Highly monodisperse, lanthanide-containing polystyrene nanoparticles as potential standard reference materials for environmental "nano" fate analysis. J Appl Polym Sci 1: 42061.

KAMOUN EA, KENAWY E-RS, CHEN X. 2017. A review on polymeric hydrogel membranes for wound dressing applications: PVA-based hydrogel dressings. Journal of Advanced Research 8(3): 217–233.

LAW K-Y. 2014. Definitions for Hydrophilicity, Hydrophobicity, and Superhydrophobicity: Getting the Basics Right. J Phys Chem Lett 5: 686−688.

LEE HJ, MICHIELSEN S. 2006. Lotus effect: superhydrophobicity. J Text I 97: 455–462.

LENOBLE B. 2007. Silicones in the Textile Industries in "Silicones in Industrial Applications" of Inorganic Polymers. Hauppage, NY: Nova Science Publishers. Dow Corning. Retrieved from https://www.dowcorning.com/content/publishedlit/Chapter5.pdf

MARMUR A. 2004. The Lotus Effect: Superhydrophobicity and Metastability. Langmuir 20(9): 3517−3519.

MIWA M, NAKAJIMA A, FUJISHIMA A, HASHIMOTO K, WATANABE T. 2000. Effects of the surface roughness on sliding angles of water droplets on superhydrophobic surfaces. Langmuir 16: 5754−5760.

OGIHARA H, XIE J, SAJI T. 2015. Controlling surface energy of glass substrates to prepare superhydrophobic and transparent films from silica nanoparticle suspensions. Journal of Colloid and Interface Science 437: 24−27.

SINGH LP, BHATACHARYYA SK, MISHRA G, AHALAWAT S. 2011. Functional role of cationic surfactant to control the nano size of silica powder. Applied Nanoscience 1: 117−122.

TADANAGA K, MORITA K, MORI K, TATSUMISAGO M. 2013. Synthesis of monodispersed silica nanoparticles with high concentration by the Stöber process. Journal of Sol-Gel Science and Technology 68(2): 341−345.

TIAN X, SHAW S, LIND KR, CADEMARTIRI L. 2016. Thermal Processing of Silicones for Green, Scalable, and Healable Superhydrophobic Coatings Adv Mat

28(19): 3677−3682.

WENZEL RN. 1936. Resistance of Solid Surfaces to Wetting by Water. Industrial and Engineering Chemistry 28(8): 988−994.

ZHANG X, ZHI D, SUN L, ZHAO Y, TIWARI, MK, CARMALT CJ, PARKIN IP, YAO L. 2018. Super-durable, non-fluorinated superhydrophobic free-standing items. J Mater Chem A **6**: 357−362.

ZHUANG A, LIAO R, LU Y, DIXON SC, JIAMPRASERTBOON A, CHEN F, SATHASIVAM S, PARKIN IP, CARMALT CJ. 2017. Transforming a Simple Commercial Glue into Highly Robust Superhydrophobic Surfaces *via* Aerosol-Assisted Chemical Vapor Deposition. ACS Appl Mater Interfaces 9(48): 42327−42335.