Ink Formulation and Printing of Superhydrophobic Paper

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Abstract

Security printing has been performed for years to combat against counterfeit documents. In this research hydrophobic silica nanoparticles are suspended into an ink and printed on paper and glass substrates. It was shown that under certain conditions superhydrophobic substrates could be created. In addition, a superhydrophobic security-feature was printed using these methods.

Introduction

Counterfeiting and Security Printing

Counterfeiting has been around for hundreds of years. For example, the British flooded the United States with fake currency to try to sow anarchy during the American Revolution, and counterfeiting has continued to increase with time. In 2009 about $250 billion dollars in counterfeit and pirated physical goods were involved in cross-border trade [1]. For example, 2011 saw $261 million in counterfeit currency removed from circulation [2]. It has been estimated that 7% of the world trade is in counterfeit goods [3]. Documents such as currency, identification cards, birth certificates, postage stamps, etc. could have a possible covert or overt signature that can only be revealed or made by a specific ink. These overt and covert markings can be used to deter counterfeiting. Thus, finding new ways and new materials to use as features on valuable items can help thwart counterfeiters.

Hydrophobicity and Hydrophilicity

Hydrophobic literally means water fearing and hydrophilic literally means water loving. Surface tension is what determines if a surface is hydrophobic or hydrophilic. Surface tension, or surface energy, is a tensile force. It is an elastic tendency of a surface to resist deformation, induced by intermolecular interaction near the surface of a material. In bulk water, surface tension is caused by the cohesive forces between each molecule. In smaller volumes the molecules coalesce to form a sphere to expose the smallest surface area relative to volume. Surface chemistry/energy and surface roughness both determine whether a droplet will bead up or spread out on a solid surface. A low energy surface is hydrophobic and a high energy surface is hydrophilic. [4]

Young's equation describes the balance of forces at the three-phase contact point of solid (s), liquid (l), and vapor (v). The contact angle, θ_Y, is defined as the tangent to the liquid-vapor interface at the three-phase contact point measured through the liquid phase [4]:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta_Y \tag{1}$$

Equation 1 assumes a smooth and homogenous surface. Real surfaces, however, have some intrinsic roughness and chemical heterogeneities. There are two ways a droplet can be in contact with a rough surface. One is the Wenzel case where there are no air pockets between the liquid and the solid surface, with an increase in contact area relative to a flat surface. The second is the Cassie-Baxter case where a droplet sits on top of the roughness on the surface trapping air pockets in the substrate roughness, reducing the effective area of contact [5, 6]. Both cases result in surface roughness scaling the current tendency of the surface; where a hydrophobic surface will become more hydrophobic and a hydrophilic surface more hydrophilic.

Superhydrophobicity

The concepts of superhydrophobicity and superhydrophilicity, were first introduced in the mid-1990s [7-10]. Superhydrophobicity specifically was introduced in 1996 and is defined as having a water contact angle greater than 150° and a contact angle hysteresis of <5-10° [7]. In this work, we will consider superhydrophobic to be a contact angle in excess of 150º without consideration of the hysteresis. The goals of this research were to i) demonstrate that an ink whose printing results in a superhydrophobic solid could be formulated, and printed; ii) to understand the mechanism behind the induced superhydrophobicity and iii) to show proof-of-concept for anti-counterfeiting by printing a security feature using these methods.

Experimental

Substrates

Two substrates were used in this research, paper and glass slides. The glass slides were standard clear glass microscope slides and the paper substrates were Avery White business cards.

Hydrophobic Nanoparticle Synthesis/Ink Formulation

Silicon dioxide (SiO_2), is naturally hydrophilic. Surface functionalization with an alkyl silane, which is a long-chained hydrocarbon that readily reacts with SiO_2, can render the surface hydrophobic. In this modified procedure, 10-20 nm silica particles were treated with trichloro(octadecyl) silane to create hydrophobic particles [11, 12]. After silanization, the nanoparticles were mixed with a material that will aid in the adhesion of the particle to the surface. In this case the adhesion promoter was polystyrene, a polymer. Four ink formulations were prepared based on the weight ratio of treated silicon dioxide to polystyrene. 25:75, 50:50, 75:25, and 0:100% by weight silica:polystyrene (PS) inks were prepared. The original literature procedure [11, 12] used ethanol as a solvent, however this created a two phase solution because of particle settling. In this research ink formulations were dispersed in toluene, because it is a good solvent for both polystyrene and the silane-treated nanoparticles. Previous research used 0.02 g silica particles per mL toluene. [11, 12] When formulating ink to print all composition herein were scaled to 0.2 g silica per 10 mL toluene.

Printing Techniques

Sono-Tek Printing

The Sono-Tek aerosol jet printer (ExactaCoat SC) is an ultrasonic spraying system designed for depositing solutions, and suspensions, including nano-particulate suspensions. Vials of toluene-based inks with the suspended silica particles were sonicated for 2 minutes. The ink was infused at 1 mL/min and the line spacing was set at 1 mm. The printhead moved at a speed of 100 mm/sec. The nozzle size was 1 mm.

Mesoscale, Maskless Materials Deposition Printing

The Optomec Mesoscale, Maskless, Materials Deposition System (M3D) aerosol jet printer was also used. The M3D places a pattern on a substrate via digital printing. An aerosol is generated and focused at the nozzle to produce feature sizes near 5 µm. Once the print head (300 micron) and line were assembled, the vial of toluene suspended silica particles was placed in the sonication bath and the nitrogen gas line was put in place. A spiral print pattern was used, printing from the outside working inward. A 10 mm x 10 mm square, or desired digital pattern was printed.

Contact Angle Measurements

Contact angle measurements were made with a Ramé-Hart model 500 goniometer using DROPImage Advanced software. There is a specific contact angle tab within the software that will take a picture and measure its angle on a given substrate. A mean measurement of the angle was recorded and the overall mean and standard deviation were determined for at least three mean contact angle measurements for each ink formulation.

Results

Initial measurements were taken of the bare paper substrate and the paper substrate printed (Sono-tek, single pass) with untreated and silane-treated SiO_2 particles (0.2 g per 10 ml toluene). The results of these experiments are shown in Table 1. The untreated glass spheres did not significantly alter the contact angle. Silane treatment increased the contact angle a small amount, but not enough to obtain a superhydrophobic (θ_Y>150º) surface.

Table 1: Paper contact angle with and without particle printing (single pass, Sono-tek).

Substrate	Mean ± Standard Deviation
Paper (bare, no printing)	46.0 ± 2.6
Paper + Untreated SiO_2 Particles	46.6 ± 3.0
Paper + Silane-treated SiO_2 Particles	60.3 ± 4.0

As particulate coating was not sufficient to give a superhydrophobic surface, a different ink formulation was required. Specifically, polystyrene (PS) was added as an adhesion promoter. Inks were made with different ratios of silane-treated silica nanoparticles and PS and printed using both a Sono-Tek aerosol jet (see Table 2) and an M3D aerosol jet printer (see Table 3). These results are both for a single pass (layer) of printed material. Figure 1 shows an example contact angle measured on a superhydrophobic surface. The results from both Sono-Tek and M3D single-pass printing are compared in Figure 2, along with the case of printing just PS with no particles. The coefficient of variation is generally less than 10% for the contact angle data, with one data set showing a much larger variation.

Table 2: Contact angle as a function of ratio of silane-treated silica particles to polystyrene (PS) on a paper substrate using Sono-Tek printing (single pass).

PS	SiO_2	Mean ± Standard Deviation
10%	90%	144.7 ± 3.0
15%	85%	163.6 ± 2.7
20%	80%	150.3 ± 0.7
25%	75%	147.8 ± 3.8
50%	50%	114.0 ± 4.6
75%	25%	104.3 ± 3.2
100%	0%	101.3 ± 8.5

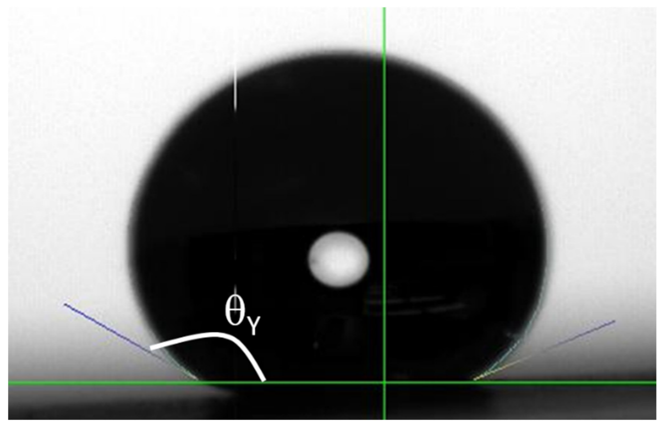

Figure 1: Contact angle of paper substrate after printing with Sono-Tek (90% SiO_2 silane treated nanoparticles:10% PS). Here the contact angle is 150º. At this contact angle, the substrate is considered a superhydrophobic substrate.

Table 3: Contact angle as a function of ratio of silane-treated silica particles to polystyrene (PS) on a paper substrate using M3D printing (single pass).

PS	SiO_2	Mean ± Standard Deviation
10%	90%	102.3 ± 4.0
15%	85%	113.5 ± 5.9
20%	80%	105.1 ± 6.4
25%	75%	115.1 ± 29.4

The single pass M3D results show that these substrates have had their contact angle raised significantly, but they are not superhydrophobic, and appear to be about the same degree of hydrophobicity as the pure polystyrene (see Figure 2). This may indicate that the silica particles were not aerosolized by the ultrasonic atomizer, so that the paper surface was only coated by polystyrene. Consequently, the Sono-Tek aerosol jet printer was used as this printer was able to reach superhydrophobicity in its printing of the SiO_2 particles/polystyrene ink.

Printing more than one pass of the ink over the surface was performed to determine how this layered approach might alter the contact angle. The results of multiple pass printing can be observed in Figure 3. In general, regardless of the number of passes, a superhydrophobic plateau in the contact angle occurs when the ratio of silane-treated silica particles to polystyrene was greater than 80:20.

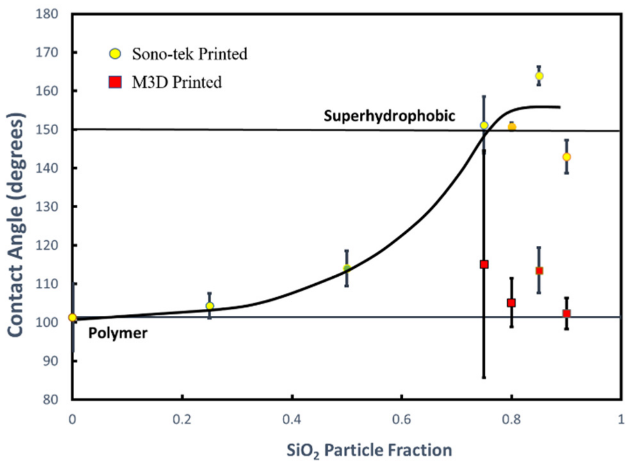

Figure 2: Comparison of contact angle of Sono-Tek and M3D printing (single pass) of silica particle (silane treated) coated paper substrates.

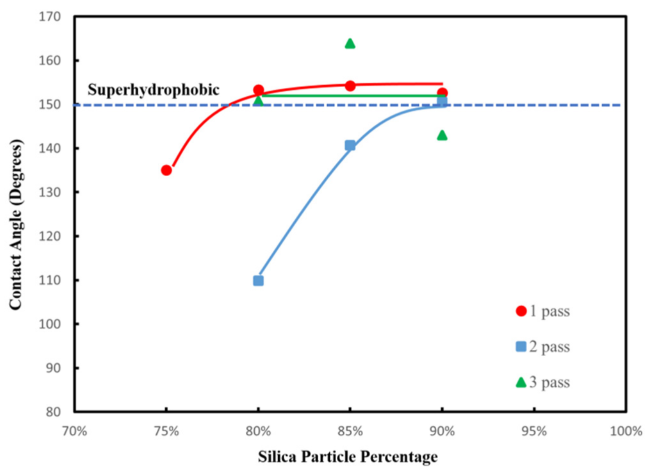

Figure 3: Effect of multiple Sono-Tek printing passes on the contact angle of silica particle coated paper substrates.

To help to understand the role of substrate roughness, the paper substrate was substituted with a glass slide (essentially flat) and the silica particle/PS ink was printed (single pass) with the Sono-Tek printer. The data for polystyrene/silica particle (silane treated) inks on glass substrates are shown in Table 4. In all cases the contact angles for the flat, glass slide substrates were considerably less than the 150º needed to obtain a superhydrophobic surface similar to that obtained with paper substrates (see Figure 4). Thus, one can conclude that the paper substrate roughness is necessary to obtain a superhydrophobic surface.

Discussion

Bare paper substrates and paper-coated with untreated silica particles are similar in terms of measured contact angle, and are relatively hydrophilic. When the silica particles were treated with silane and then printed on the paper substrate, the contact angle increased but still was still not indicative of a superhydrophobic surface (see Table 1). As PS thin films typically have a water contact angle of ~86º [13], the 0:100% value indicates only partial PS coverage. Yet, to achieve a superhydrophobic state, the binder (PS) was required, which along with the extra roughness from the silica particles, yielded a superhydrophobic surface.

Table 4: Contact angle as a function of ratio of silica particles to polystyrene (PS) on a glass slide substrate using Sono-Tek printing (single pass).

PS	SiO_2	Mean ± Standard Deviation
10%	90%	105.1 ± 10.2
15%	85%	107.1 ± 16.1
20%	80%	104.1 ± 4.9
100%	0%	30.2 ± 1.4

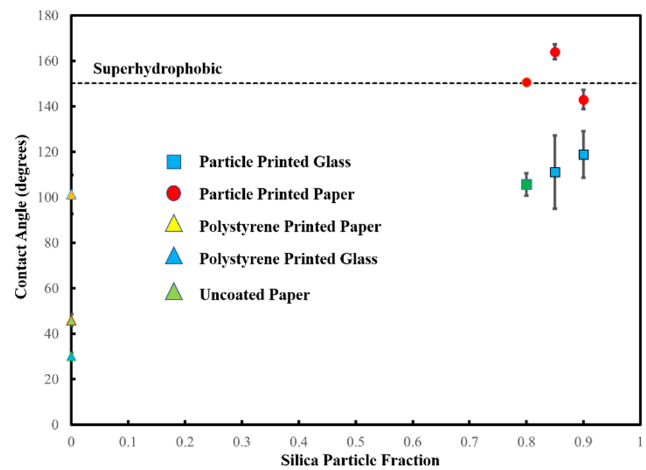

Figure 4: Comparison of contact angle of Sono-Tek printed (single pass) silica particle (silane treated) coated paper and glass slide substrates.

The ink formulation that gave a superhydrophobic surface on paper was utilized on smooth glass slides. It was found that the printed glass slides did not become superhydrophobic, but did increase the glass substrate hydrophobicity (see Figure 4). Therefore, it can be concluded that the intrinsic paper roughness is an important factor in obtaining a superhydrophobic surface.

To help understand the roughness effects on the printed surfaces scanning electron microscopy (SEM) was utilized. SEM images of the bare paper substrate as can be seen in Figure 5. The image shows the expected inherently rough paper surface with interwoven fibers. The SEM image of the paper with the printed formulation that gives a superhydrophobic substrate is shown in Figure 6. This image shows that the nanoparticles were agglomerated in clumps with preferential deposition along the edges and between the paper fibers. The same printed ink formulation on the glass slide (see Figure 7) showed similar clumping of nanoparticles, however the absence of any underlying roughness led to a more uniform distribution of clumped particles on the glass slide than was seen on the paper substrate.

The roughness effects can be estimated from the data gathered and applying either the Wenzel ($\cos\theta_{measured} = r\cos\theta_{smooth}$) or Cassie-Baxter ($\cos\theta_{measured} = \Sigma f_i \cos\theta_i$) equations. From the Wenzel equation, the increase of contact line length of r≈5 for the paper substrates. The Cassie-Baxter equation application indicates that a water drop contacts about f≈15-30% of the paper substrate.

The final research effort involved demonstrating proof-of-concept of a security feature based upon the inks formulated. In other words, the desire was to create a feature that would allow for authentication testing or for document verification. To accomplish this task the M3D printer was used, as it allows printing of digital image files, whereas the Sono-Tek printer does not. Recall, that early research presented here questioned the M3D's ability to adequately sonicate the nanoparticles. Care was taken during printing to ensure that this occurred, and a quick response (QR) code was printed on paper using the ink formulation. Figure 8 demonstrates one manner in which the security mark could be used. First, blue ink was placed on a laboratory Kimwipe. The Kimwipe was gently rubbed over the printed QR code printed with ink that had a measured 163º contact angle. The ink base soaked into the paper, causing the dark background shown in Figure 8. Given the 'water-hating' properties of the printed material the QR code then becomes visible. In other words, the water-based ink does not adhere to the printed, superhydrophobic QR code.

Future research will include surface analysis using a profilometer. This analysis will help to quantitatively assess the roughness of the substrate. This quantification will be very useful and help to determine whether the Wenzel or Cassie-Baxter case best describes the roughness effect on the contact angle. Finally, future research will also attempt to quantify the relative adhesion of the printed features on the paper substrates.

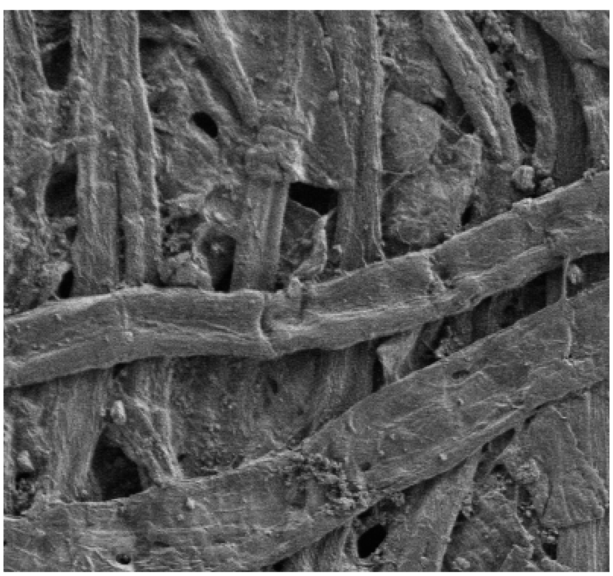

Figure 5: SEM image of bare paper substrate.

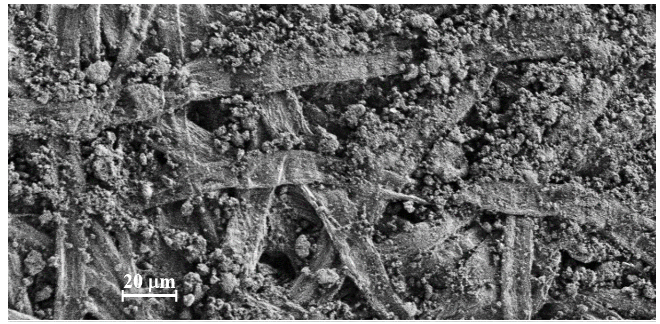

Figure 6: SEM image of 90% silane treated silica nanoparticles:10% PS on a paper substrate, Sono-Tek (single pass).

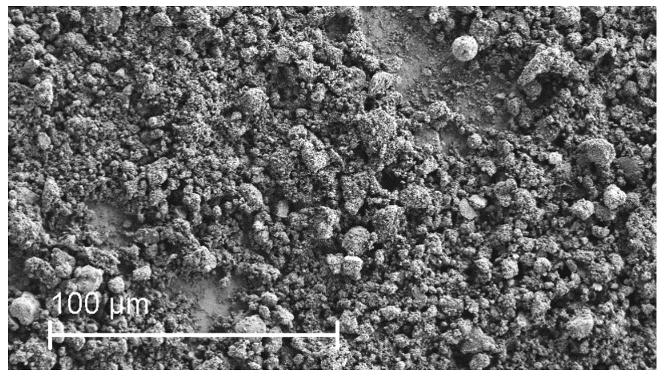

Figure 7: SEM image of 90% Silica-10% PS printed on a glass slide.

Figure 8: QR code security mark printed using an M3D aerosol jet printer after wiping with an aqueous solution containing a colored ink.

Conclusion

An ink formulation was created that demonstrated the ability to print superhydrophobic features on paper. The ink included nano-scale SiO_2 particles treated with an alkyl silane surface treatment and used polystyrene as an adhesion promoter. The same formulation printed on glass increased the hydrophobicity of the glass substrate, but did not reach the superhydrophobic condition. SEM images of the printed substrates revealed clumping of the nanoparticles, with preferential deposition along and between the paper fibers. Given the lack of fibers and inherent roughness on the glass such preferential deposition of the clumped particles was not observed. Thus, it was concluded that the superhydrophobic condition on paper was a result of the fibrous substrate acting in conjunction with the ink formulation. Finally, proof-of-concept of a printed security feature on paper was demonstrated using the above concepts.

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