Transparent superhydrophobic surfaces using a spray coating process☆

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ABSTRACT

One significant maintenance problem and cost associated with solar energy conversion systems is the soiling due to the accumulation of dust and other pollutants. In this work, we describe a scalable approach for applying antisoiling coatings based on superhydrophobic (SH) silica particles using a spray coating process. A large water contact angle (WCA) is one of the characteristics of excellent SH surfaces and because of the low surface energy and low adhesion forces the soiling rate is reduced. Our findings indicate that the WCA depends strongly on the ratio of the polymer binder and the nanoparticles. The nanoparticle surface coverage of the spray coated samples was substantially improved after rinsing with solvent. This process tended to remove large aggregates and excess polymer binder and further increased the WCA by allowing exposure of the functionalized nanoparticles. The durability of the SH coatings was enhanced when the substrate was pretreated with polymer binder and an optimal curing time between 30 and 60 min. The abrasion tests of the SH coatings we report in this study showed that the WCA decreased from $\sim 166°$ to $\sim 157°$ after exposure to 2.6 g of sand. Such coatings will help reduce costs of periodic cleaning of solar energy conversion systems (photovoltaic panels and concentrated solar mirrors).

1. Introduction

Although the availability of solar energy has variability depending on time and location it remains one of the attractive energy resources [1]. Maintaining clean surfaces and decreasing the accumulation of dust and other pollutants is important for increasing the efficiency of systems for solar energy conversion [2,3] such as photovoltaic panels and solar mirrors. Dust is a term generally applied to solid particles with diameters less than 500 μm [4]. Accumulation of a film of dust is considered an environmental stimulus, third in importance after irradiance and air temperature [5]. Previous studies [6] have reported the soiling rate in different regions by studying declines in power plant performance and found that system efficiency due to soiling declines by an average of 0.2% per day without rainfall in dry climates. In addition, in photovoltaic systems rain and soiling by salty aerosols can lead to substantial leakage currents [7]. Using antisoiling coatings shows potential to reduce dust accumulation and maintain higher system efficiency. Requirements for low-soiling surfaces include hydrophobicity, low surface energy, and non-stickiness [8], weather and abrasion resistance and high transparency [9].

An inspiration for self-cleaning surfaces is the lotus leaf, which exhibits superhydrophobic (SH) properties with a water contact angle (WCA) of about 160° and a roll-off angle of 2–4° [10,11]. Self-cleaning approaches that use of superhydrophilic [12] and superhydrophobic [13–15] coatings has been reported before but the lack of a coating scalable process has limited to smaller areas. SH coatings have low surface energy and low adhesion forces [16] which reduces the rate of dust accumulation and the superhydrophobicity facilitates near-complete cleaning of the surface during rain events. Durable anti-soiling coatings are still not available and it is a topic of on-going research to address this need. [9].

The transparent antisoiling coatings we describe in this work were deposited with a scalable spray coating process which produced thin layers of highly transparent SH silica nanoparticles bound to the substrate using a polymer binder. The spray deposition of the nanoscale nanostructured features on the surface due to the nanoparticles (50–200 nm) can also provide antireflective properties [17]. Producing superhydrophobic and superhydrophilic nanoparticle films with increased optical transmittance has been reported by multiple groups [15,18,19] and the surface feature sizes was kept below 200 nm in

order to minimize light scattering at the shortest transmission wavelength (~ 300 nm).

The application of durable SH coatings on large surfaces has been hampered by the lack of an appropriate scalable deposition process. Developing a spray coating process that can produce transparent and durable layers was the goal of our study. In the past, we have developed spin coating deposition methods that were used to optimize the formulations of the transparent SH coatings [19]. Some of the best performing coatings (high WCA) were produced with the spin coating process using Cerakote [20] as the polymer binder [19].

2. Experimental

2.1. Materials

Glass samples were used as substrates for the deposition of nanoparticle films by spray coating. The glass samples were cleaned by sonication in acetone, iso-propyl alcohol (IPA), and deionized water for 10 min. For the coating process, we used a chemical solution that consisted of 3 g Cerakote (MC-156 High Gloss Ceramic Clear) [20], 60.0 g of Acetone (or IPA), 0.3 g of commercial hydrophobic silica nanoparticle (Aerosil® r8200, fumed silica), and 0.3 g of fluorinated silica nanoparticles [19]. For some of the prepared samples, we used a combination of IPA with parachlorobenzotrifluoride (PCBTF). The solutions were sonicated in an ice bath and subsequently centrifuged at 4500 rpm. Silica nanoparticles that were functionalized with hydrocarbon precursors are compatible with hydrocarbon-based solvents used for their dispersion.

We developed a spray coating system to deposit silica nanoparticle film on glass substrates (with dimensions up to 210 mm × 297 mm) using 5 psi of atomization pressure with 4 layer cycles. The injection flow rate of the nanoparticle solution was 0.0278 ml/s, with a nozzle speed of 50 mm/s and a raster spacing of 25 mm. The spray gun had a diameter of 0.5 mm and a high efficiency air cap. The spray coated substrates were vertically rinsed with fresh organic solvents (e.g. acetone or IPA). The excess binder polymer was solvent-rinsed within 30 min of the coating process and before curing the polymer binder. The rinsed samples were dried at 60 °C for overnight in a furnace and subsequently allowed to cool to room temperature. In order to achieve a uniform solvent rinse, we also used spin rinsing with IPA solvent for 30 s at 1000 rpm. Silica nanoparticle thin films were deposited on glass substrates using colloidal silica solutions under ambient conditions. The silica coated samples were dried at 65 °C for 10 min in a furnace and then allowed to cool to room temperature. Some of the samples were pretreated with polymer binder and the curing time was varied prior to spray coating the binder/nanoparticle solution.

The sprayed coatings exhibited good superhydrophobic behavior with water WCA > 150°, rolling angle (RA) of < 10°, and a WCA hysteresis (difference between the advancing and receding contact angles)) of < 15°. In addition to durability and optical transparency, for a surface to have excellent self-cleaning properties, high WCA and low WCA hysteresis are necessary [19].

2.2. Sample characterization

The surface morphology of each surface was investigated by scanning electron microscope (SEM). WCA measurements were performed with a tensiometer, and a spectrophotometer (UV–vis–IR) was used for transmittance measurements over the wavelength range of 300–1100 nm at normal incidence.

In order to assess the durability of the antisoiling coating we have performed falling sand abrasion testing using a commercial falling sand tester. The tester conforms to the ASTM D968 standard for abrasion resistance by falling abrasive [21], but the test method was adapted for resistance of the SH coatings to multiple of annual dust accumulation. The diameter of the sand reservoir is 20 cm with 60° funnel and a guide
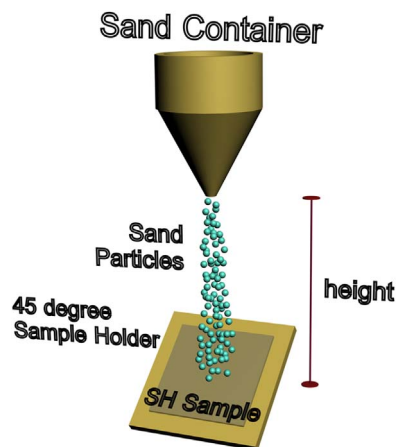

Fig. 1. Schematic of the experimental setup for the falling sand abrasion testing. The height was 100 cm impacting an area of ≈ 2.86 cm².

tube with 100 cm length. The specimen receptacle has a removable viewing window and a 45° angled specimen holder. A schematic of the experimental setup for the falling sand abrasion testing is shown in Fig. 1. The inside diameter of the guide tube on falling sand test apparatus is 1.91 cm, so the abraded area A on the test specimen will be ≈ 2.86 cm², assuming no divergence of the flow as the sand leaves the tube. An earlier study reported a dust collection of about 2.5 g/m²/day between April and June [22] or equivalently 0.09 g/cm² per year. Arizona dust particles have a size distribution range is 0.8–300 μm, with the particle distribution peaking at 55 μm [23]. For a guide tube of 100 cm in length (and ignoring the air resistance), the exit velocity of the falling sand particles is about 4.4 m/s (or 16 km/h). We consider this a typical wind speed in Arizona [24]. This impact velocity is roughly equivalent to the average wind speed in the desert southwest of the U.S.A. For the falling sand abrasion test we used ISO 12103-1, A4 Coarse Test Dust with average particle diameter of 55 μm.

3. Results and discussion

The chemical solution that was used for the spin coating [19] was based on 3 g of Cerakote, 3 g of PCBTF, 20 g of IPA and 0.2 g of silica nanoparticles produced high quality SH surfaces (WCA > 165°). However, for the spray coating process we found that this concentration of binder was high and tended to mask or overcoat the silica nanoparticles, which resulted in a coating that was not superhydrophobic. We found that it was necessary to reduce the concentration of the polymer binder (Cerakote) and soften the spray coating of the nanoparticle solution. SEM images for a binder/nanoparticle mass ratio, R_m of 15 are shown in Fig. 2. The coatings in Fig. 2 were applied using a rastering sprayer system and were reproducible between successive samples in terms of surface morphology and WCAs. The excessive binder interferes with the nanoparticle functionality and rinsing with solvent tended to remove the excess resulting in smoother coatings.

Cerakote/nanoparticle formulations based on reduced amounts of binder were synthesized and sprayed on glass substrates. For reference, the WCA of Cerakote coated substrates was measured which was 78.4 ± 2.4°.

Using polymer binder and functionalized nanoparticles increases the WCA. SH coatings were prepared using 0.1 g fumed silica (Aerosil) [25], 0.1 g fluorinated silica, 20 g IPA and varied the polymer (Cerakote) binder amount resulting in binder/nanoparticle mass ratio, R_m of 2.5, 5, and 10. The WCA of coatings as a function of R_m are shown in Fig. 3. A decrease in R_m (decrease in polymer binder) was found to result in a systematic increase in the WCA values. For an R_m of 2.5 the WCA increased to ~ 142°. However, as R_m decreases there is also a noticeable decrease in durability for the SH coating. These coatings