

# Water-Based, Nonfluorinated Dispersions for Environmentally Benign, Large-Area, Superhydrophobic Coatings

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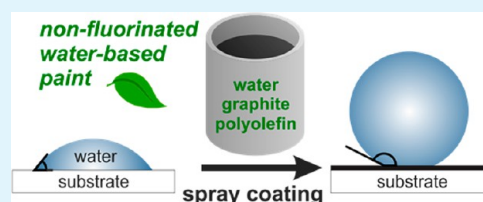
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## S Supporting Information

**ABSTRACT:** Low-cost, large-area, superhydrophobic coating treatments are of high value to technological applications requiring efficient liquid repellency. While many applications are envisioned, only few are realizable in practice due to either the high cost or low durability of such treatments. Recently, spray deposition of polymer–particle dispersions has been demonstrated as an excellent means for producing low-cost, large-area, durable, superhydrophobic composite coatings/films; however, such dispersions generally contain harsh or volatile solvents, which are required for solution processing of polymers as well as for dispersing hydrophobic nanoparticles, thus inhibiting scalability due to the increased cost in chemical handling and environmental safety concerns. Moreover, such coatings usually contain fluoropolymers due to their inherent low surface energy, a requirement for superhydrophobicity, but concerns over their biopersistence has provided an impetus for eliminating these chemicals. For spray coating, the former problem can be overcome by replacing organic solvents with water, but this situation seems paradoxical: Producing a highly water-repellent coating from an aqueous dispersion. We report a water-based, nonfluorinated dispersion for the formation of superhydrophobic composite coatings applied by spray on a variety of substrates. We stabilize hydrophobic components (i.e., polymer, nanoparticles) in water, by utilizing chemicals containing acid functional groups (i.e., acrylic acid) that can become ionized in aqueous environments under proper pH control ( $\text{pH} > 7$ ). The functional polymer utilized in this study is a copolymer of ethylene and acrylic acid, while the particle filler is exfoliated graphite nanoplatelet (xGnP), which contains functional groups at its periphery. Once spray deposited and dried, the components become insoluble in water, thus promoting liquid repellency. Such coatings can find a wide range of applications due to their benign processing nature as well as the variety of substrates on which they can be deposited.

**KEYWORDS:** graphene, wettability, water-based liquid-repellent coating, superhydrophobic, polyolefin, nonfluorinated, spray



## I. INTRODUCTION

Spray deposition of polymer composite coatings that contain high-aspect ratio filler particles has been demonstrated as a low-cost, large-area process for modifying the wettability (e.g., superhydrophobicity,<sup>1–4</sup> superoleophobicity<sup>5</sup>), electrical conductivity,<sup>4–7</sup> and EMI shielding<sup>6,7</sup> properties of a variety of surfaces. The purpose of the filler particles is dual, namely, to impart surface texture in the dry coating—a requisite for water repellency—and introduce additional functionality. With regards to liquid repellency, a low surface-energy polymer ( $\sim 20 \text{ mJ m}^{-2}$ ) must be incorporated into the coating, a general requirement of any liquid repellency treatment. This is conveniently achieved by utilizing fluoropolymers, for example, fluoroacrylic copolymers, poly(tetrafluoroethylene), and so forth. However, concerns over the byproducts of fluoropolymer degradation, for example, long-chain perfluorinated acids (PFAs), which have a documented ability to bioaccumulate,<sup>8,9</sup> as well as the potential adverse effects that PFA maternal concentrations can have on human offspring,<sup>10,11</sup> have led to a

shift in the manufacture and usage of fluoropolymers. One common PFA of particular concern is perfluorooctanoic acid (PFOA). In 2006, the EPA introduced its PFOA Stewardship Program and invited eight major fluoropolymer and telomer manufacturers to commit to eliminating precursor chemicals that can break down into PFOA; in one case, DuPont introduced so-called *short-chain chemistry*, whereby the length of perfluorinated chains within polymers are kept below a threshold in order to avoid degradation into PFOA. In other applications, usage of fluoropolymers in products that come in sustained contact with the human body or in disposable items intended for landfilling after consumption must be minimized. For these applications, polymers such as polyolefins (PE) are far more preferable. Where the environment is concerned, *hydrophobic* polymers intended for application by spray should

Received: October 3, 2013

Accepted: December 2, 2013

Published: December 2, 2013

ideally be water-borne, so as to minimize the usage of harmful volatile organic compounds (VOCs)—a common, *nontrivial* problem with coatings aiming to achieve superhydrophobicity upon deposition. Water dispersion of hydrophobic polymers could be facilitated by introducing pendant acid functional groups that can be charge-stabilized by increasing the pH of the dispersing medium (water);<sup>12,13</sup> in short, acid functional groups ionize, thus creating charge repulsion, and ultimately facilitating stabilization. Acid functional groups offer an additional advantage, as they also act to promote adhesion with polar surfaces.

The choice of filler particles is quite restrictive, as the particles should possess a high-aspect ratio, re-entrant characteristics (i.e., high curvatures), low surface energy, and still be dispersible in water. One such filler is fatty amine salt modified nanoclay<sup>14</sup> (i.e., organoclay), which is highly hydrophobic in its native state, but can be dispersed in water by reducing the pH due to its cationic surfactant functionalization.<sup>15</sup> However, for the case of water-based PE dispersions with acid functionality or anionic surfactants (emulsifiers), the dispersions are of a basic character rendering cationic surfactant modified fillers (i.e., organoclay) infeasible. Another common filler—exfoliated graphite (e.g., graphene, few layer graphene (FLG), or exfoliated graphite nanoplatelet (xGnP))—might be useful due to its ability to form said acid functional groups at the periphery of its basal planes without forming oxygen groups normal to the plane (i.e., not becoming graphene/graphite oxide) by large-area processing.<sup>16</sup> Maintaining limited oxygen functionality allows the filler to stay relatively hydrophobic, while still being water-dispersible under proper (high) pH conditions. This is an important point, meaning that no ionic surfactant functionality is required to play the role of dispersant (when in the dispersion) or surface energy reducer (when cast in the coating), as is the case with nanoclays—potentially reducing the fabrication cost. There is also a myriad of other non-high-aspect ratio, hydrophobic fillers that might benefit from a similar approach (e.g., hydrophobic fumed silica); however, exploring other fillers is out of the scope of the present study.

Approaches to utilizing graphene/graphite in superhydrophobic applications are reported in the literature and a few will be briefly discussed here to demonstrate applicability. In a recent report,<sup>17</sup> a dispersion consisting of colloidal graphite and polytetrafluoroethylene was spray cast and sintered to form the basis for a conductive, thermally stable, water-repellent coating. Other approaches to utilizing graphite—or its exfoliated form, graphene—to form superhydrophobic films have included aerogels,<sup>18</sup> poly(vinylidene fluoride) composites,<sup>19</sup> and Nafion blends.<sup>20</sup> Graphene oxide films can also be superhydrophobic when modified by octadecylamine; however, this is not suitable for our application for the same reason that organoclays cannot be used.<sup>21</sup> Work regarding wettability tuning for graphene films to water has been done (e.g., superhydrophobic to superhydrophilic), but it relied on chemisorption of acetone to defects in graphene reduced from graphene-oxide.<sup>22</sup> In all of these studies, none of the systems was water-based, and some contained some type of fluoropolymer.

Approaches to nonfluorinated superhydrophobic coating treatments are numerous; however, from a water repellency standpoint, such treatments are not ideal. The surface tensions of typical end bonds in organic hydrophobic coating treatments are ranked from highest to lowest as  $-\text{CH}_2 > -\text{CH}_3 > -\text{CF}_2 > -\text{CF}_2\text{H} > -\text{CF}_3$ , with fluorine-containing bonds having the

lowest surface tension.<sup>23</sup> Replacing  $-\text{CF}_3$  with  $-\text{CH}_3$  chemistries introduces more stringent requirements (e.g., more roughness) when designing coating surface texture, if superhydrophobicity is the main goal. Holtzinger et al. provided a description of available methods of fluorine-free superhydrophobic coating treatments as well as their intricacies.<sup>24</sup> Achieving a superhydrophobic coating with nonfluorine chemistry is relatively simple though when compared with developing *water-based superhydrophobic coating treatments*.

Very few works have been reported on water-based superhydrophobic coating treatments from spray, and even fewer have been fluorine-free. Reports on hydrophobic coatings from water-based dispersions have been around for some time;<sup>25</sup> however, interest in superhydrophobic coating treatments from all-aqueous dispersions is a relatively recent research endeavor. As one example, a recent patent application claims a superhydrophobic coating realized by spray deposition of an all-aqueous dispersion consisting of a fluoroacrylic copolymer, bentonite nanoclay, and water.<sup>15</sup> Researchers have looked into the use of rare earth metals—of which some are known to be hydrophobic—in an all-aqueous sol-gel process to achieve hydrophobic coatings (e.g., lanthanum);<sup>26</sup> however, these coatings were not superhydrophobic and their use—as their name implies—may be cost prohibitive and therefore limited in terms of industrial scalability.

We report herein, for the first time, an approach to produce an all-water-based, nonfluorinated superhydrophobic surface treatment from a sprayable PE-xGnP dispersion. Hydrophobic components are stabilized in water by their acid functional groups via increased pH. Such an approach to water-repellent coatings is expected to find wide application within consumer products aiming to achieve simple, low-cost, large-area, environmentally benign superhydrophobic treatments. It is emphasized that xGnP is employed here due to its ability to be simply functionalized through its exfoliation process, but that any hydrophobic, high-aspect ratio filler with similar chemistry can also be used in its place. As one possibility, one can modify nanoclay by an anionic surfactant and follow the same procedures listed here for processing xGnP to achieve similar results.

## II. EXPERIMENTAL SECTION

**A. Materials.** Exfoliated graphite nanoplatelets (xGnP Brand Nanoplatelets; grade C 300) were obtained from XG Sciences (average particle thickness  $\sim 2$  nm, average particle diameter  $< 2$   $\mu\text{m}$ , surface area  $300$   $\text{m}^2$   $\text{g}^{-1}$ ). Polyolefin (PE) dispersion (42 wt % in water; HYPOD 8510, pH  $\sim 9$ ) was obtained from DOW Chemical.<sup>13</sup> The dispersion contains a blend of two types of polyolefin: polyethylene-acrylic acid copolymer ( $\sim 40\%$ ) and polyethylene-octene copolymer ( $\sim 60\%$ ); the former copolymer stabilizes the dispersion. Ammonium hydroxide (29% in water) was obtained from Fisher Scientific, and formic acid (97% purity) was obtained from Alfa-Aesar. Two pH buffer solutions, one with pH = 10 (borax/sodium hydroxide; Sigma Aldrich) and the other with pH = 4 (potassium hydrogen phthalate/formaldehyde; Sigma Aldrich) were used to test the superhydrophobic state of the coatings against high and low pH aqueous solutions.

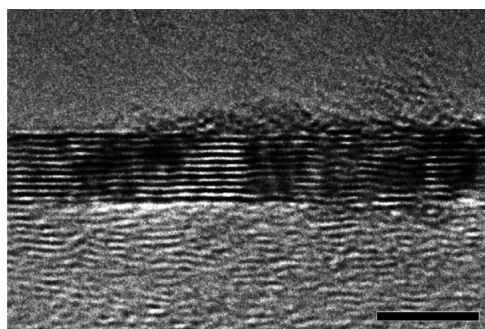
**B. Procedure.** The procedure began by first combining the ammonium hydroxide and xGnP in a 20 mL vial (refer to Table 1 for specific concentrations). The mixture was placed in a sonication bath (output power 70 W; frequency 42 kHz; Cole-Parmer, model 08895-04) for several minutes until a paste was formed. Next, water was added to the mixture and probe sonication (750 W, 13 mm probe dia., 20% amplitude, 20 kHz frequency, Sonics & Materials, Inc.) was performed for several minutes. Once stabilized, the PE dispersion (42

**Table 1.** Example Dispersion Used for Creating PE-xGnP Composite Coatings

ingredient	concn (wt %)
PE	2.8
xGnP	0.8–10.0
ammonium hydroxide, 29% in water	6.7
water	89.7–80.5

wt % in water) was added to the xGnP-NH<sub>3</sub>(aq)-H<sub>2</sub>O mixture and was bath sonicated for 1 h or until stable. It should be noted that a high quality dispersion can also be achieved by adding the PE dispersion to the xGnP-NH<sub>3</sub>(aq)-H<sub>2</sub>O suspension while under intense mechanical mixing with a stir bar (>1200 rpm; StableTemp Ceramic Hot Plate). In this approach, for a 20 mL vial, it is important to keep the mass of the dispersion ~10 g so as to maximize the intensity of mixing. Once a stable dispersion is produced, it is spray deposited (Paasche VLS, siphon feed, 0.73 mm nozzle) onto either glass slides, paper, or aluminum foil and dried at 80 °C in an oven for 1 h. In order to form high quality coatings, it is necessary to heat the substrates while they are being coated in order to avoid excess water from collecting on the surface, a problem not typically encountered with VOCs, such as acetone. In our application, we utilized a heat gun (Proheat Varitemp PH-1200, 1300W max) to heat the substrate—in between spray coating applications—from a distance of ~10–20 cm.

Wettability characterization of the spray-deposited coating was done by measuring advancing and receding contact angle values by the sessile drop method, whereby 5–10 μL volumes of water were dispensed (advancing measurement) and removed (receding measurement) through a flat tipped needle placed near the substrate. Contact angle measurements were made with images captured with a high-speed, backlit image acquisition setup (Redlake MotionPro). A new spot was used on the substrate for each individual measurement. Several probe liquids were used: deionized water, acid buffer solution (pH = 4), and base buffer solution (pH = 10). Transient apparent contact angle values ( $\theta^*$ ) were also measured for the aforesaid probe liquids, whereby a single droplet was placed onto the coated substrate and the contact angle value was measured at one minute intervals for a duration of ten minutes. Morphological characterization of the spray-deposited coatings was done with a Hitachi S-3000N scanning electron microscope (SEM) after the samples were coated with a 4 nm layer of Pt/Pd. Characterization of the particle filler xGnP was done with a JEOL JEM-3010 transmission electron microscope (TEM) to determine the degree of xGnP exfoliation. According to the manufacturer, xGnP is in granular form and requires mechanical agitation to become exfoliated. For TEM preparation, xGnP (0.013 g) was added to formic acid (10 g) in a 20 mL vial. The suspension was probe sonicated (13 mm probe; 20% amplitude; 1.0 kJ energy delivered to probe), mechanically mixed at room temperature for 10 min, and bath sonicated for 30 min; the suspension was then dispensed dropwise onto a holey carbon grid for subsequent TEM image analysis. Figure 1 presents a side-view TEM image of a typical

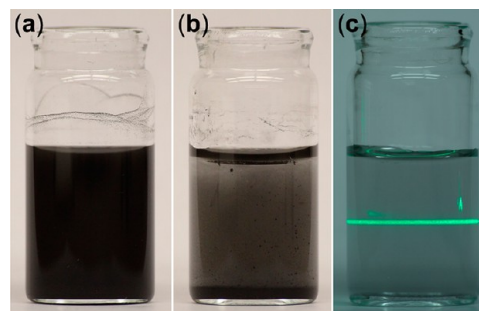
**Figure 1.** High magnification TEM image of an xGnP platelet demonstrating a platelet thickness below 5 nm. Scale bar is 5 nm.

xGnP platelet demonstrating adequate exfoliation (~10 layers of graphene). According to the manufacturer, the xGnP filler comes with a variety of oxygen containing functional groups at the edges of the platelet as a result of the exfoliation process; such functional groups include carboxyl, lactone, pyrone, hydroxyl, and carbonyl. The weight concentration of oxygen generally increases with the degree of platelet exfoliation—and for the type of xGnP used in this study—the concentration is around 2 wt %, as stated by the manufacturer.

### III. RESULTS AND DISCUSSION

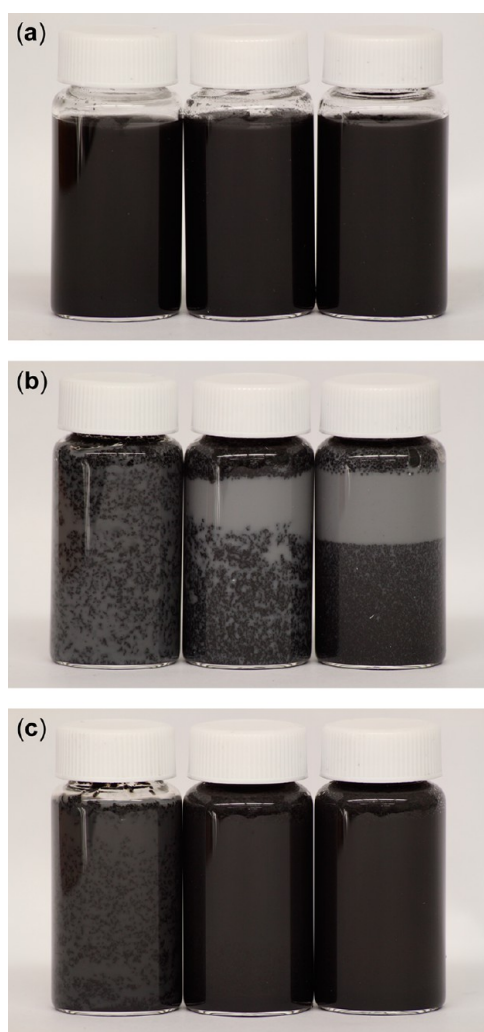
In general, for commercial applications of paint or coating treatments, the stability of the dispersion is an extremely important property, and in this study, the pH of the overall dispersion is most critical. Figure S1 (Supporting Information) presents images of three side-by-side 15 mL vials, all containing water and PE. The difference between the contents of the three vials is in their pH values. The dispersion in vial 1 is slightly basic, vial 2 basic, and vial 3 acidic; vial 3 is phase separated. The PE utilized in this study has acrylic acid functionality, a so-called acid functional group, which allows it to become water dispersible under basic conditions, and stay dispersed even at elevated pH values. In the case of vial 3, the addition of acetic acid no longer allows the acrylic acid groups to retain their charge, in turn phase separating the solution.

Figure 2a presents an image of a suspension formed by xGnP (hydrophobic) in water. Since these particles are inherently

**Figure 2.** Suspensions of 0.1 wt % xGnP in water with (a) no electrolyte, and (b) electrolyte (0.1 wt.% NaCl). (c) Scattering effect demonstrated on a diluted (0.002 wt.%) xGnP–water suspension.

hydrophobic, their apparent stabilization in water without the aid of dispersants is likely due to electrostatic repulsion (i.e., ionization of acid functional groups). Figure 2b presents an image of an xGnP-water suspension containing an electrolyte, which acts to suppress the electrical double layer over the particles and destabilize the suspension; this is a characteristic property of lyophobic colloids stabilized by electrostatic repulsion, in accordance with Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.<sup>27</sup> Figure 2c presents an image of the diluted suspension undergoing laser irradiation (simple laser pointer) perpendicular to the point-of-view; note the light scattering, which is characteristic trait of a fine, well dispersed suspension, thus supporting the colloidal nature of the xGnP-water suspension. In fine suspensions, light scattering is more intense for shorter wavelengths (i.e., blue, green); this effect gives the appearance of a blue/green color, and is commonly referred to as the Tyndall effect.

Figure 3 presents a sequence of images of the PE-xGnP dispersion after each major processing step (i.e., probe sonication of xGnP-water suspension, addition of PE, bath sonication of the final dispersion); ceteris paribus, the pH of the

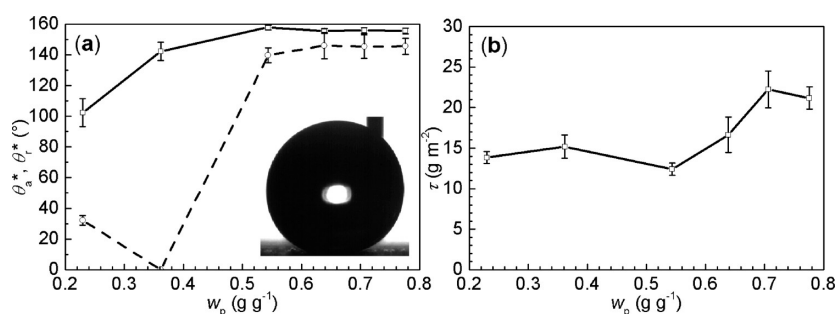


**Figure 3.** (a) xGnP-water suspensions in 20 mL glass vials with varying concentration of ammonium hydroxide (left vial 0 wt %, middle vial 0.3 wt %, right vial 2.2 wt %). (b) Vials from (a) with 1 g of a 42 wt % PE dispersion in water added to each. (c) Vials from (b) after 60 min of bath sonication. Note the apparent stability of the dispersions with higher pH values (i.e., middle, right vials).

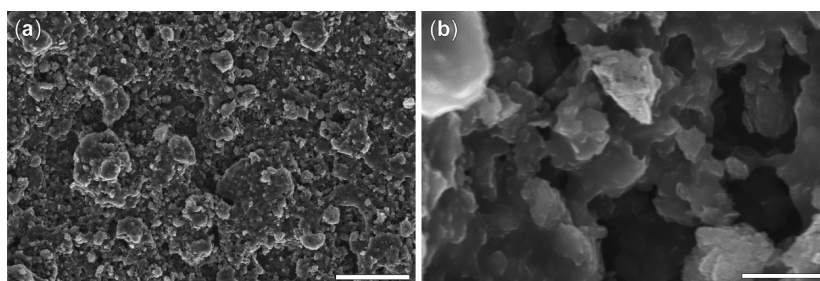
individual dispersions increases from vial-to-vial (i.e., the left vial has the lowest pH, the right vial has the highest pH). Figure 3a presents three xGnP-water suspensions after probe sonication (first processing step). Based on visual observation, the stability of the dispersions did not appear to vary

significantly from neutral to basic conditions. According to a previous report of water suspensions containing carboxylic-acid functionalized graphene,<sup>27</sup> increasing the pH of the suspension only acts to increase its stability, with the zeta potential changing from  $-30$  mV for pH  $\sim 6.1$  to  $-43$  mV for pH  $\sim 10$ . Since the xGnP-water suspension is to be stabilized by a similar mechanism, the outcome that no change in colloidal behavior is observed for increased pH is thus expected. Figure 3b shows the same three vials after the addition of the PE solution. In all cases, the xGnP aggregates to produce an unstable dispersion that requires the third processing step: bath sonication. The dispersions (in vials) after that final processing step are depicted in Figure 3c; the left vial (dispersion pH  $\sim 7$ ) is unstable, while the middle and right vials (pH  $> 7$ ) are stable. It appears that in the case of vial 1, the xGnP undergoes irreversible aggregation due to the addition of PE. Aggregation of exfoliated graphite in water is a frequent problem encountered when reducing graphene oxide to graphene in water with hydrazine, due to the hydrophobicity of graphene.<sup>27,28</sup> This problem can be addressed by controlling the pH of the suspension in order to utilize nonreactive edge functional groups (e.g., carboxylic acid) to charge stabilize the suspensions.<sup>27</sup> The energy required to exfoliate, or in this case redisperse, graphite can be quite high owing to the extremely large surface area required to separate as well as the strong van der Waals interactions between adjacent platelets.<sup>27</sup> Regarding the stability of xGnP in aqueous solutions, previous work (described above) has shown that aqueous suspensions of graphene oxide and chemically converted graphene have zeta potentials  $< -30$  mV (stable) for pH values ranging from 7 to 11; decreasing pH results in a lower magnitude of zeta potential and hence in less stable dispersion.<sup>27</sup> We hypothesize that the increased pH allows for charging of the edge functional groups on xGnP (higher magnitude of zeta potential) and enables it to be redispersed much easier than for neutral conditions (pH = 7).

Figure 4a presents a plot of advancing and receding water contact angles on spray deposited PE-xGnP coatings as a function of filler particle concentration in the dry composite coating. We define the filler particle concentration as a mass fraction,  $w_p = m_{\text{xGnP}} / (m_{\text{xGnP}} + m_{\text{PE}})$ , where  $m_{\text{xGnP}}$  and  $m_{\text{PE}}$  are the respective masses of xGnP and PE in the composite coating. As observed in previous spray coating studies<sup>29,30</sup>—for example, in the classic Johnson and Dettre<sup>31</sup> experiment—at low  $w_p$  values, advancing contact angles increase while receding contact angles decrease, leading to a widening contact angle hysteresis ( $\Delta\theta = \theta_a^* - \theta_r^*$ ). After sufficient filler loading, the



**Figure 4.** (a)  $\theta_a^*$  (advancing contact angle, □) and  $\theta_r^*$  (receding contact angle, ○) vs.  $w_p$  (xGnP mass fraction in the dry composite coating). (b) Coating add-on level ( $\tau$ ) vs.  $w_p$  for the coatings characterized in (a). Inset in (a) shows image of an advancing water contact angle measurement ( $\sim 2.0$  mm diameter droplet) on a PE-xGnP coating with  $w_p = 0.64$ .



**Figure 5.** SEM images of a spray deposited coating with  $w_p = 0.54$ . (a) Low magnification ( $50 \mu\text{m}$  scale bar); (b) high magnification ( $5 \mu\text{m}$  scale bar). This specific coating had the minimum value of  $w_p$  where the Cassie–Baxter wetting state was exhibited by water droplets.

receding contact angle value abruptly jumps and becomes comparable with the advancing contact angle value (severely reducing contact angle hysteresis), indicating increased water droplet mobility and ultimately liquid repellency at  $w_p = 0.64$ , where  $\Delta\theta = 9^\circ$ . The wettability transition from low  $\theta_a^*$  and high  $\Delta\theta$  to high  $\theta_a^*$  and low  $\Delta\theta$  is commonly referred to as the Wenzel<sup>32</sup>-to-Cassie–Baxter<sup>33</sup> transition, and is usually associated with a large increase in liquid droplet mobility. As is widely reported in the spray coating literature, coating morphology as a result of spray processing and filler inclusion can, under proper circumstances, produce highly textured surfaces;<sup>34–37</sup> when coupled with low-surface energy polymers, such coatings are capable of becoming superhydrophobic, and in some cases superoleophobic.<sup>5,29,36</sup> Figure 4b shows the individual add-on levels of coating ( $\tau$ ) required to achieve the desired wetting properties presented in Figure 4a. All of the coating add-on levels are in the range  $10\text{--}25 \text{ g m}^{-2}$ , which is a typical level required to achieve superhydrophobicity using spray coating of untextured substrates.

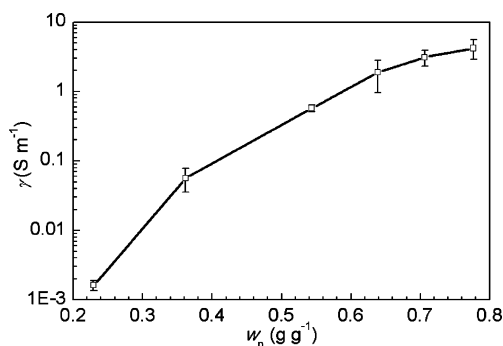
Figure 5 presents two SEM micrographs (increasing magnification a-to-b) of a superhydrophobic coating with  $w_p = 0.54$ , which marks the lowest filler concentration level above which the transition from Wenzel<sup>32</sup> to Cassie–Baxter<sup>33</sup> wetting state occurred (Figure 4a). While the surface is highly textured, it also has certain roughness features (e.g., hierarchical, re-entrant, porous) that contribute to liquid repellency better than other surfaces would.<sup>38,39</sup> This is the type of surface texture required to induce a wettability transition from Wenzel to Cassie–Baxter wetting state (i.e., liquid repellency), and has been reported in previous studies of liquid repellent coatings applied by spray.<sup>29,37</sup>

While morphological and wettability analysis offer valuable insight on the repellent property of a composite coating, they provide little insight on the long-term performance or the durability of the coating, which are very important properties from the practical standpoint. Figure S2a,b (Supporting Information) shows a PE-xGnP composite coating on glass ( $w_p = 0.64$ ) being exposed to an impinging water-jet, with a velocity of  $\sim 5 \text{ m s}^{-1}$  for about 1 min. Even at this high flow-rate, the coating is not observed to delaminate or degrade. After drying, only a moderate loss of liquid repellency performance is observed (Figure S2c,d;  $\theta_a^* = 153^\circ$ ,  $\Delta\theta = 15^\circ$ ). An additional characterization technique that assesses coating durability is the so-called “tape peel” test. This test was performed on the same sample after the water-jet test. Standard Scotch tape, a pressure sensitive tape, was pressed onto the superhydrophobic PE-xGnP coating and manually removed (Figure S3a–e); only a small portion of the coating was removed by the adhesive tape (Figure S3e). The superhydrophobic property is not lost ( $\theta_a^* = 154^\circ$ ) and the contact angle hysteresis ( $\Delta\theta$ ) is still  $12^\circ$  after

testing (Figure S3f–h). The above tests demonstrate moderate durability of the superhydrophobic property in the present coatings.

Since the coating components were “soluble” or “dispersible” in basic solutions ( $\text{pH} > 7$ ) prior to spray deposition, an important consideration is whether or not the deposited (dry) coating is soluble or repellent to such solutions. Figure S4 presents a plot of  $\theta^*$  (static apparent contact angle) on a PE-xGnP coating ( $w_p = 0.64$ ) vs the time duration of the measurement, that is, a measure of how the contact angle of a single droplet evolved in time. For coatings that are soluble in a given probe liquid, one would expect that a droplet should transition from a Cassie–Baxter to a Wenzel wetting state, and therefore,  $\theta^*$  should decrease sharply as time increases. For a 10 min measurement with a basic buffer solution ( $\text{pH} = 10$ ), the apparent contact angle,  $\theta^*$ , remained greater than  $147^\circ$ ; therefore, a transition to a Wenzel state is not observed, and the PE-xGnP coating is “practically” insoluble. As a control, the same experiments were performed with water and an acid buffer solution, and similar performance was observed for the transient contact angle characterization (Figure S4). Ultimately, the coating is insoluble to water, acid buffer solutions and basic buffer solutions. Insolubility of the PE-xGnP composite coating to basic buffer solutions can be possible only if the acid functional groups of PE do not come into contact with the solution. Many hydrophobic polymer–water suspensions (e.g., polystyrene) rely on the presence of ionizable comonomers, such as acrylic acid, where the degree of ionization of the comonomer is critical in determining the size and stability of the polymeric particles.<sup>40</sup> The polymer films that result can remain hydrophobic through two possible mechanisms: (1) the ionizable groups (e.g., acid functional groups) orient toward the substrate, thereby enhancing adhesion; (2) some of the ionizable molecules are vaporized during the coating drying process, since some of these may not have participated in the polymerization process. In the case of the PE-xGnP composite, the ionizable groups may also orient toward the xGnP platelets. Both of these mechanisms, which could be acting simultaneously, provide plausible explanations for why the dry PE-xGnP composite coating is insoluble in water or buffer solutions.

Since electrically conducting graphite was utilized as a major component of this composite, another important property is quantified by electrical conductivity measurements. Figure 6 is a plot of coating electrical conductivity ( $\gamma$ ) vs  $w_p$ ; increasing concentrations of xGnP result in rising conductivity of the composite coating (measured by the two-probe method). While the conductivity levels are relatively low,<sup>6,7</sup> likely owing to nonalignment of graphite platelets as well as the porosity of



**Figure 6.** Coating electrical conductivity ( $\gamma$ ) vs PE-xGnP coating composition,  $w_p$ .

the coating, such formulations may still be useful for antistatic coatings in packaging applications.

Finally, we conclude with some remarks on the use of ammonium hydroxide as a pH adjuster in the water-based, nonfluorinated dispersion. From a processing and safety perspective, the choice of using ammonium hydroxide for stabilizing the dispersion is deliberate. This compound is commonly used in many household cleaning supplies, and the U.S. Food and Drug Administration (FDA) classifies it as a “generally recognized as safe” (GRAS) substance for use in a direct human food ingredient—for pH control—in part due to its integral nature in metabolic processes.<sup>41,42</sup> In the present study, the dispersions utilized to synthesize superhydrophobic coatings had a measurable concentration of ammonium hydroxide solution. We generally utilized dispersions that had ~2 wt % ammonium hydroxide; however, in some applications, this concentration may still be prohibitive. In some cases though, we were able to generate stable dispersions with ~0.3 wt % ammonium hydroxide, as demonstrated by Figure 3c, thus promising material savings and improved safety with this dispersion. Addition of xGnP particles in the aqueous polymer solution causes interaction of the acrylic acid monomer with the graphene surface, decreasing the ionic stability of the polymer in water. This destabilizes the polymeric dispersion if ionization of the acrylic acid is not increased. This was done by adding ammonium hydroxide to the graphene solutions a priori. Specifically, ammonium hydroxide promotes the ionization of acrylic acid further through increased pH of the dispersion, thus resulting in stabilization.<sup>40</sup> Such concentrations approach those used in standard window cleaning solutions (~0.1–1.0 wt % ammonium hydroxide).<sup>43</sup> Minimizing the concentration of the pH adjuster could form the basis for future work on optimizing water-based coating treatments.

#### IV. CONCLUSION

We report for the first time an all-aqueous, fluorine-free dispersion that when spray-deposited and dried as a thin film, forms a superhydrophobic, self-cleaning coating. A combination of water-based polyolefin (hydrophobic) solution with a stable exfoliated graphite nanoplatelet (hydrophobic) water suspension constitute the sprayable dispersion. Both components are charge stabilized in water through pH modification. At the optimum xGnP mass fraction of 0.64, the coatings feature contact angles exceeding 150° and contact angle hysteresis below 10°. In addition, the coatings are electrically conducting with conductivity exceeding 1 S m<sup>-1</sup>. The present study offers new insights on synthesizing fluorine-free coatings that are not

only environmentally friendly, but also well suited for manufacturing platforms where all-aqueous formulations are preferred.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

Images and figures including the stability of the polyethylene–acrylic acid copolymer under various pH conditions; water-jet and tape peel tests and subsequent wettability characterization; transient contact angle measurements on superhydrophobic coatings with probe liquids of varying pH. This material is available free of charge via the Internet at <http://pubs.acs.org>

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##### Notes

The authors declare no competing financial interest.

#### ■ ACKNOWLEDGMENTS

This material is based upon work supported by Kimberly-Clark Corp. T.M.S. thanks Joseph M. Mates (UIC), Jared Morrisette (UIC), and Zachariah Rabatah (UIC) for their assistance in the water jet test, tape peel test, and PH buffer characterization.

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