Article

Asphaltene-Derived Graphene Quantum Dots for Controllable Coatings on Glass, Fabrics, and Aerogels

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ABSTRACT: Graphene quantum dots (GQDs) derived from natural asphaltene byproducts can produce controlled hydrophobic or hydrophilic interfaces on glass, fabrics, and aerogels. A set of facile solvent extraction methods were used to isolate and chemically prepare materials with different surface functionalities from a commercially derived asphaltene precursor. The organic-soluble fraction was used to create hydrophobic and water-repellent surfaces on glass and cotton fabrics. The GQD solutions could also penetrate the pores of a silica aerogel, rendering it hydrophobic. Alternatively, by extracting the more polar fraction of the GQDs and oxidizing their surfaces, we also demonstrate strongly hydrophilic coatings. This work shows that naturally abundant GQD-containing materials can produce interfaces with the desired wettability properties through a straightforward tuning of the solvent extraction procedure. Owing to their natural abundance, low toxicity, and strong fluorescence, asphaltene-derived GQDs could thus be applied, in bulk, toward a wide range of tunable surface coatings. This approach, moreover, uses an important large-scale hydrocarbon waste material, thereby offering a sustainable alternative to the disposal of asphaltene wastes.

INTRODUCTION

Asphaltenes are a class of compounds making up nearly 15% of heavy crude oil. They render the oil highly viscous and must, therefore, be chemically separated from it. This produces a large quantity of chemical waste with little market value and significant worldwide disposal concerns.[1] Developing viable applications for asphaltene is thought to be a way to reduce the quantity of chemical wastes from heavy oil production.[2] One such application could arise from the development of controlled hydrophobic or hydrophilic films or coatings from asphaltene wastes. Hydrophobic surface treatments and coatings are used in a vast array of applications. For example, hydrophobic coatings are important in the textile and automotive glass industries. These coatings frequently involve application of poly(dimethylsiloxane) (PDMS) polymer-based films[3] or, alternatively, a chemical silanization treatment. PDMS is relatively straightforward to apply to glass but is gradually removed because the polymer is physisorbed onto the surface. In comparison, silanization involves the covalent bonding of molecular and oligomeric silanes (often fluorosilanes) to glass,[4] leading to a more robust coating. However, silanization requires in situ use of flammable solvents or even boiling nitric acid to obtain optimum results.[5,6] Moreover, there is persistent concern over the chemical and environmental safety of currently available commercial products, especially for textile spray-on hydrophobic coatings. One important example is perfluorooctanesulfonate, a bioaccumu-

lating toxin which is a key component of consumer sprays routinely applied to fabrics to render them stain-resistant.[7] Concerns associated with these common surface treatments have motivated industry and academics alike to search for safer, more environmentally responsible textile coatings. There are numerous options, but many involve multistep chemical treatments[8] and some have significant drawbacks.[9]

Hydrophilic treatments also have widespread applications in microfluidic and droplet technologies in applications ranging from greenhouse agriculture[10] to health care[11] and water treatment.[12] Several types of hydrophilic coatings or treatment processes are frequently used. For example, amphiphilic molecules such as poly(vinyl alcohol) (PVA) essentially convert hydrophobic surfaces to hydrophilic ones. Plasma-oxygen treatment or immersion of glass surfaces into a strongly oxidizing solution (e.g., "piranha solution", a mixture of sulfuric acid and hydrogen peroxide) exposes the native surface −OH groups and is widely employed to create hydrophilic interfaces. However, these treatments are costly and present safety concerns.
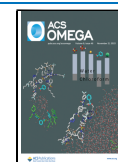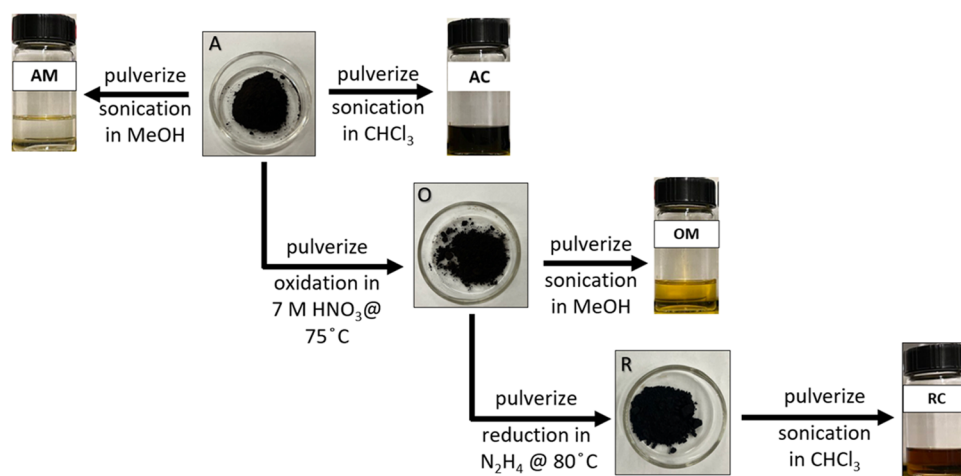
Figure 1. Illustration of the process used to prepare type-AM, -AC, -OM, and -RC GQDs.

A variety of nanoparticle-based hydrophobic coatings have recently appeared in the literature and have been shown to feature several potential or realized advantages.[8] They can roughen surfaces at the nanometer scale, affecting the interfacial tension. They can also be prepared from comparatively benign materials, such as oxides or carbon. Composite coatings from silanized silica nanoparticles are especially common because they use nontoxic and environmentally friendly silica or fumed silica precursor particles.[13,14] Other proposed options include zirconia[15] or titania[16] nanoparticle hybrid composites that also have low toxicity. Silicon nanoparticles have been recently treated with both hydrophobic and hydrophilic surface groups to control their interfacial properties in novel lithium battery anodes.[17] Carbon-based nanomaterials are especially interesting in this regard, especially for hydrophobic coatings.[18−20] This is because of their generally benign chemistry,[21] comparatively low environmental risk,[22] and straightforward chemical requirements to prepare the coatings.

An abundant and inexpensive natural source of graphene quantum dots (GQDs) for hydrophilic or hydrophobic surface treatments could thus be important for the development of economical and environmentally safer surface treatments.[23−26] Here, we show that particulates derived from natural asphaltene waste streams can be used to form either hydrophobic or hydrophilic coatings on glass, textiles, and aerogels. This approach uses an abundant, low-cost natural source of GQD-based materials to produce simple spray-on or immersion coatings. The GQDs are preselected via a solvent extraction method from an asphaltene precursor and can then be directly applied to the desired surface to produce an interface with either polar or nonpolar properties. Although the particles are only physisorbed onto the surface of glass, cotton, or aerogels, they are comparable in this sense to many commercial spray-on products. Moreover, the GQD composite materials are highly fluorescent, suggesting potential secondary applications toward high visibility road safety,[27] sensing, and decorative materials.[28] The idea of using asphaltene-derived GQDs for specialized surface coatings has several attractive features, including (i) the diversion of an abundant waste stream toward functional products, (ii) the believed low toxicity of carbon-based nanoparticles compared with the chemicals found in many current commercial hydrophobic coating products, and (iii) the ability to tailor the materials toward either hydrophilic or hydrophobic coatings, a feature that is not commonly accessible with other surface treatment chemicals.

■ EXPERIMENTAL SECTION

Synthesis. All reagents were used as received, unless otherwise stated. Nitric acid (certified ACS Plus) and hydrazine monohydrate (98+%) were purchased from Fisher Chemical and Alfa Aesar, respectively. Other reagents including methanol (high-performance liquid chromatography (HPLC) grade), heptane (reagent grade), chloroform (HPLC grade), and toluene (HPLC grade) were obtained directly from BDH VWR Analytical. 0.2 μm Nylon and PTFE syringe filters were supplied by VWR International. The methods employed were modified based on our previous report[29] and are summarized herein. Bitumen from the Alberta oilsands was first mixed with heptane (1 g of bitumen for each 40 mL of solvent), sonicated for 50 min, and allowed to settle for 24 h. Then, 75 vol % of the supernatant filtered using Whatman filter paper #2 and fresh solvent with 10% of the volume of the original solution was added to the mixture. The mixture was then sonicated again for 45 min, followed by settling for 15 h. The mixture was filtered again, and the resulting asphaltene precipitate was washed with fresh heptane until it was nearly colorless. The solids were then dried under a vacuum and ground using a mortar and pestle to produce a fine asphaltene powder (A) as the starting material. The subsequent synthesis steps are illustrated in Figure 1. Portions of A were placed in a single-neck round-bottom flask and oxidized in HNO$_3$ (7 M, 100 mL) at 75 °C for 12 h. The prepared suspension was then cooled to room temperature. The particles were then separated by vacuum filtration (0.22 μm MCE membrane) and rinsed with deionized (DI) water until the liquid leaving the filter was pH-neutral. The resulting asphaltene oxide (O) product was dried in a vacuum oven at 75 °C for 12 h, pulverized using a mortar and pestle in order to minimize agglomeration, and stored in a standard glass vial. Finally, 1.0 g of O was dispersed in DI water (100 mL) and then sonicated for 3 h. Hydrazine monohydrate (1.0 g) was added to the solution, and the mixture was stirred at 80 °C for 12 h to produce reduced asphaltene oxide (R). The powder was separated by vacuum filtration and washed with DI water at room temperature. The product was deagglomerated (pulverized) using a mortar and pestle to produce dry R powder. Finally, GQDs were

synthesized from A, O, and R powders following further ultrasonication and solvent extraction. 100 mg of each powder was dispersed in either methanol or chloroform. The dispersions were sonicated for 3 h, causing the particles to be suspended into the organic solvents. The supernatant was extracted after the settlement of unreacted precursors, filtered through 0.2 μm nylon syringe filters in the case of methanol (M) samples or PTFE filters for chloroform (C) samples, and then stored in glass vials. These samples are referred to according to the GQD type (A, O, or R) and the solvent (M or C) (Figure 1).

In short, GQD-like carbon nanomaterials were obtained from asphaltene and its oxidized and reduced derivatives by using a facile ultrasonication method. To obtain GQDs with different surface groups, asphaltene (A) was separated from bitumen by using heptane. Asphaltene was then oxidized by using nitric acid to produce asphaltene oxide (O). The resulting asphaltene oxide was reduced by using hydrazine monohydrate to produce reduced asphaltene oxide (R). These carbon precursors with different surface groups (i.e., A, O, and R) were used to produce different GQDs in organic solvents with different hydrophobicity.

Aerogels. GQD-free silica alcogels were prepared using base-catalyzed sol−gel processing using a literature procedure.[30] Tetramethoxysilane (TMOS), methanol, and DI water with volume ratio of 2.6:5.9:1 were mixed and sonicated for 1 min, followed by the addition of catalytic amounts of ammonium hydroxide (3.4 μL). Approximately 600 μL of silica solution was transferred into plastic syringes, wrapped with parafilm, and aged for 24 h. After the gel was formed, the solvents were exchanged with anhydrous ethanol every 4 h over 24 h to remove the ammonium hydroxide catalyst. The as-prepared silica alcogel was submerged in 5 mL of the GQD solution (1 g/mL) for 48 h. Under these conditions, the particles enter the silica alcogel host to form infused alcogels. This hybrid material was placed in a home-built CO_2 supercritical dryer with acetone as a solvent to be exchanged with liquid CO_2 over a period of ~12 h prior to the final drying procedure. Finally, the dryer assembly was heated, and the temperature and pressure were raised to 40 °C and 8.3 MPa, respectively, above the critical temperature and pressure of liquid CO_2 (31 °C and 7.4 MPa, respectively), leaving a GQD-infused silicon aerogel monolith.

Characterization. To ensure reproducibility and continuity with previous experiments, the GQDs were characterized by using transmission electron microscopy (Hitachi H-9500), scanning electron microscopy (Hitachi S4800 FESEM), and Fourier transform infrared spectroscopy (Shimadzu IRTracer FTIR). For cotton fabrics, we also performed a standard water repellency spray test.[31] Water contact angle measurements were performed with deionized water at room temperature by using an FTA-200 contact angle analyzer.

Optical Properties. The optical absorption and fluorescence of the solutions were measured by using standard fiber-optic methods. For absorption spectra, a solution of low concentration of synthesized GQD-based powder (0.06 mg/mL) was placed in a fused silica cuvette, and the absorbance was determined using a deuterium tungsten lamp as the light source. A spectrum of the neat solvent sample was used as the blank. For fluorescence spectra, the combined 352 and 364 nm lines of a UV-optimized Ar^+ ion laser were used as an excitation source. Sample fluorescence was measured with an

intensity- and wavelength-calibrated miniature fiber-optic spectrometer.

Sample Preparation and Coating. For glass surfaces, fused silica substrates were prepared by washing them in methanol and then allowing them to dry in air. The GQDs in either methanol or chloroform solutions were simply added into a standard 50 mL commercial spray bottle, and the suspension was sprayed directly onto the silica slide until no uncoated regions remained. The solvent was then allowed to evaporate. Samples were subsequently washed in one of three solvents (toluene, methanol, or chloroform) to qualitatively evaluate the adhesion of the particles on the underlying surface.

To prepare pretreated hydrophobic surfaces, silica slides were first soaked in piranha solution (danger: extremely corrosive) at 85 °C for 20 min and subsequently washed with Milli-Q water and ethanol and then dried at 125 °C in an oven for 1.5 h to remove excess adsorbed water.[32] The resulting dry surfaces were immersed into 0.5 vol % octadecyltrichlorosilane (OTS, 98.9%, Acros Organics, Fisher Scientific) in hexane solution for 13 h in a sealed container and then washed with hexane, acetone, and ethanol, followed by air drying at room temperature. The hydrophobic slides were stored prior to use in the experiments. For fabric testing, a plain twill-weave cotton fabric was washed several times with ethanol and dried at 70 °C for 2 h, then spray-coated with GQD solution, and then cured for 3 h at 130 °C in air. Finally, for aerogels, the as-prepared silica alcogel was submerged in 5 mL of the solution (1 g/mL) for 48 h, as described above.

■ RESULTS AND DISCUSSION

The naturally derived hydrophilic or hydrophobic GQDs were isolated via a solvent extraction method. When dispersed in methanol, toluene, or chloroform, the resulting suspensions could be readily used to spray-coat a variety of surfaces. Here, we focus on particles of type-AC or -RC for hydrophobic surfaces and type-AM or -OM for hydrophilic surfaces (see Figure 1). FTIR spectra of the particles (Figure 2a) show
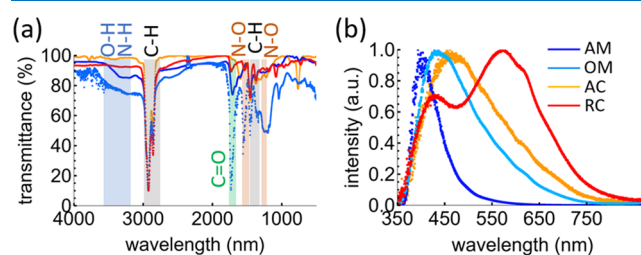

Figure 2. (a) Representative FTIR (a) and photoluminescence (b) spectra for all GQDs types (AM OM, AC, and RC).

characteristic absorptions at 2850−2950 and 1365−1475 cm^{-1} corresponding to C−H stretching and bending vibration characteristics of GQDs, respectively. A sharp absorption related to C=O stretching at 1700−1715 cm^{-1} and a broad absorption associated with O−H stretching at 3450 cm^{-1}[33] are also evident in the spectrum of type-OM and -AM GQDs, indicating an oxidized surface. The suspensions were strongly fluorescent, showing blue-green emission that is often observed for GQD and carbon-based nanomaterials (Figure 2b);[34] we also note a broad, featureless absorption band extending into the ultraviolet (Figure S3). Brightfield transmission electron microscopy (TEM) imaging indicated the presence of small

particles (range 3−15, mean 6.4 nm) with 0.27 and 0.35 nm lattice spacings consistent with those of graphene[35] (Figures S1 and S2). Other samples were previously characterized by TEM analysis.[29]

When applied to clean glass surfaces, the GQDs had an obvious effect on the water contact angle (Figure 3), which
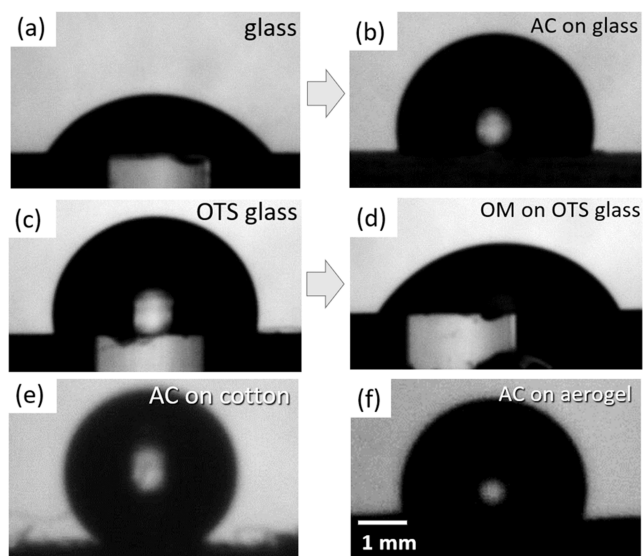

Figure 3. Photographs showing water droplets on various surfaces: (a) on clean glass, (b) on clean glass converted to a hydrophobic surface with a coating of type-AC GQDs, (c) on a clean glass surface-treated with octyl-triethoxysilane (OTS), (d) on OTS converted to a hydrophilic surface after a subsequent coating of type-OM GQDs, (e) on a plain cotton fabric spray-coated with type-AC GQDs, and (f) on a silica aerogel after infusing with type-AM GQDs. The experiments were repeated 5 times to estimate the error, which turned out to be ±2°.

increased from 52 to 102° after a light spray-coating of type-AC particles (Figure 3a,b). Subsequently washing the hydrophobic surface three times in water had negligible effects on the contact angle, consistent with the GQDs being adsorbed onto the glass surfaces. In contrast, for substrates treated with type-AM or -OM materials, the contact angle on the glass stayed nearly unchanged from that of the clean glass surface. Therefore, we pretreated a glass slide with OTS (see the Experimental Section) to obtain an initial contact angle of 101°. A light spray-coating of type-OM or AM solutions subsequently reduced the contact angle to ∼57°, indicating the

recovery of a hydrophilic interface (Figure 3c,d). The contact angle was similarly unchanged after three washings with toluene. Thus, these asphaltene-derived nanoparticles can be concentrated by using a straightforward solvent extraction method to obtain nanomaterials with the desired interfacial properties. Surprisingly, the sliding angle was not significantly improved (i.e., lowered) with any of the GQD coatings, suggesting that other factors such as the interfacial resistance may play a more dominant role on the inclined glass surfaces.[36]

Figure 1 shows how type-AC GQDs can be converted to type-OM GQDs by oxidation (see the Experimental Section), at which point they become hydrophilic, similar to type-AM. Finally, type-OM materials were exposed to a strong reducing agent and then extracted into chloroform. These "type-RC" particles yielded a contact angle of 87°, showing that the hydrophobic property was recovered, although the contact angle did not fully regain that of the original type-AC particles. Because the hydrophilic or hydrophobic character can be switched with oxidation and reduction, the overall yield of GQDs with the desired surface property can be increased via chemical treatment. In other words, instead of simply removing GQDS with each type of surface from the original asphaltene materials, one can concentrate them by oxidation or reduction.

On cotton fabrics, the hydrophobic effect after applying the type-AC spray was even more striking (Figure 3e), likely because of the fibrous nature of the interface. Water droplets were strongly repelled from the fabric, with a contact angle of 137°. In contrast, when sprayed with type-OM hydrophilic GQDs, water immediately permeated through the entire fabric thickness. As before, washing the material in plain water did not remove the hydrophobic effect of type-AC particles, and it was moreover difficult to submerge the fabric at all (Figure S4). The treated and untreated fabrics were also tested for water repellency using the standardized AATCC22 method.[37] For the untreated cotton fabrics, the AATCC test value was 0, indicating complete wetting of the upper and lower surfaces. However, for the AM-treated cotton fabrics, the measured AATCC22 value was 70, indicating that the GQDs produced modest water repellency and that water did not permeate the fabric. The cotton fabric with the spray-on GQDs also repelled tea, milk, wine, and an aqueous rhodamine 6G solution (Figure 4). The fabric is moreover strongly blue-fluorescent due to the incorporated GQDs (Figure 4b). The combined water-repelling and fluorescent properties are sought after in clothing used by emergency workers;[27] in fact, a hydrophobic fluorescent fabric was first reported in 2022, which used a
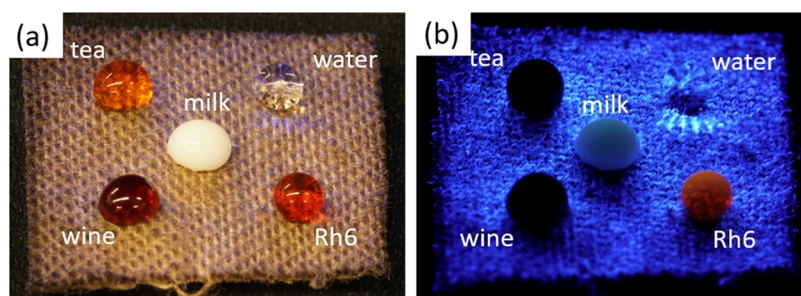
Figure 4. Photographs of various droplets (tea, water, milk, wine, and a solution of rhodamine 6G in water) on cotton fabrics treated with type-AC GQDs. (a) An image taken in room light and (b) taken under a 365 nm filtered UV lamp. The fabric is blue-fluorescent because of the incorporated GQDs, and the rhodamine 6G (Rh6) droplet is orange. The other droplets are nonfluorescent. The fluorescence image was taken in two parts (bottom and then top) and stitched together to ensure a more uniform focus throughout the image.
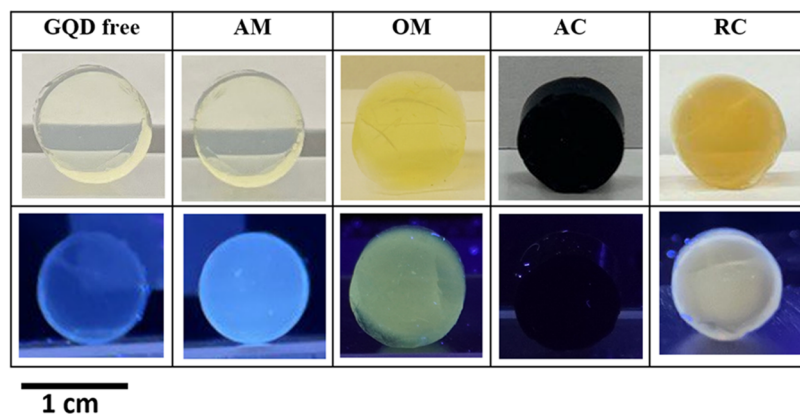
Figure 5. Unfiltered photographs of GQD-infused aerogels under ambient (top row) and UV light (bottom row).

rather complicated multichemical process to bind both a dye and a hydrophobic amine group to a cotton textile.[28] GQDs have the potential to fulfill both of these qualities (hydrophobicity and strong fluorescence) simultaneously.

We next examine the wettability of silica aerogels with hydrophobic GQD coatings. Hydrophobic silica aerogels have applications that include environmental cleanup,[38,39] drug delivery,[40] corrosion protection,[41] and enzyme encapsulation.[42] Moreover, when placed in an aqueous solution, hydrophilic silica aerogels are subject to rapid structural collapse, limiting their applications in many common situations.[43] Silica aerogels also absorb humidity gradually resulting in a slow decrease in optical transparency.[44] Numerous approaches have been developed to synthesize hydrophobic aerogels.[43] Standard TMOS (or similar) fabrication processes, as used here, have the advantage of being widely applied in aerogel synthesis, but rendering them hydrophobic can require extensive post-treatment.[45]

The as-produced silica aerogels prepared for the present study showed the typical porous structure (Figure S5) and quickly absorbed water: a droplet placed on the surface is instantly subsumed into the aerogel volume. In order to change the interface property, we submerged silica alcogels in 5 mL of the GQD solution (1 g/mL) for 48 h and dried the prepared GQD-infused alcogel, as described in the Experimental Section. The GQD-infused aerogels became fluorescent (Figure 5) and, overall, retained good transparency, except for the sample infused with type-AC GQDs (Figure 5). The contact angle was measured on a flat aerogel surface; for aerogels infused with type-AC GQDs, the angle was 101° (Figure 3f). In contrast, an aerogel infused with type-OM GQDs was fluorescent but retained its hydrophilic character and immediately adsorbed any water placed on its surface. Moreover, when placed in a water bath, the hydrophobic aerogel (type-AC) floated; whereas, the hydrophilic one (type-OM) immediately submerged. Aerogels with type-RC GQDs became similarly hydrophobic and water-repelling.

Much attention has been paid to the properties and applications of carbon-based nanomaterials such as nanotubes and graphene that make them excellent candidates for hydrophobic surface coatings and surfactants.[19,20,46] Carbon-based nanomaterials have also been surface-engineered for supercapacitor applications,[47] nonionic organic adsorbates,[48] and fluorescent sensors for aromatic amino acids.[49] While the field is undeniably crowded, the present work established some new features of asphaltene-GQD-based surface coatings. For

example, one can produce a large range of surface properties with the same abundant, naturally occurring GQD precursor material. This means that interfaces with preset hydrophobicity or hydrophilicity can be produced using a facile chemical method that readily lends itself to bulk production. The method capitalizes on a common hydrocarbon waste stream to produce functional materials with selectable surface properties. Comparing type-AM and -AC GQDs, the solvent extraction process with natural asphaltene can produce suitably hydrophilic or hydrophobic properties even without subsequent surface treatments. Moreover, features such as water repellency of carbon nanomaterials have not been reported before. Obviously, there is room for further improvement; for example, a larger range of contact angles is likely possible with more involved or "cleaner" preparation methods, especially given that asphaltene and its derivatives contain impurities that can affect the material properties. Also, the adsorption of the GQDs onto the different surfaces is relatively weak, but binding agents are a common part of industrial surface coatings.[50]

■ CONCLUSIONS

The development of potential applications for asphaltene compounds is one way to reduce the ever-increasing quantity of chemical wastes from hydrocarbon production.[2] We found that GQDs and associated products derived from asphaltene waste streams can be readily applied to the formation of either hydrophilic or hydrophobic surfaces via a facile spray-coating method. We showed that hydrophobic glass, textiles, and aerogels were easily formed using asphaltene-derived GQDs extracted from a chloroform solvent. The materials were stable against washing in pure solvents of opposite polarity, suggesting that the particles were fairly well physisorbed onto the host material. At the same time, GQD-coated textiles became moderately water-repellent and strongly blue-fluorescent. Cotton fabrics demonstrated good self-cleaning properties against tea, water, milk, wine, and a solution of rhodamine 6G. Similarly, good hydrophobic effects were produced on aerogels infused with type-AC or -RC materials. In contrast, the naturally derived particles extracted into methanol (type-AM or -OM) isolated a strongly hydrophilic coating behavior. Fabrics spray-coated with these GQDs quickly absorbed moisture, and aerogels infused with type-OM GQDs immediately sank instead of floating on water. These results show that GQD-based carbon materials can be prepared in bulk with a wide range of surface polarities for the desired

applications. Moreover, the source materials are a common, naturally occurring waste product from hydrocarbon extraction, suggesting a potentially important use for materials diverted from industrial wastes. Because impurities are likely present (especially type-AC), further purification and isolation of more narrowly distributed carbon-based nanoparticles are likely to enhance these properties in future.

◼ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c04942.

> TEM image; size distribution analysis; absorbance spectra; photo of the AC-infused cotton fabric floating on water, and SEM image of AC-infused aerogels (PDF)

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Notes

The authors declare no competing financial interest.

◼ ACKNOWLEDGMENTS

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