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Controlling water contact angle on carbon surfaces from 5° to 167°

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The interaction of liquid water with graphenic carbon surfaces is important for nanotube dispersion and processing [1], nanotube fluidics [2,3], aqueous phase sorbent applications [4], protein adsorption and cell behaviour on carbon implant surfaces [5], and the rates of cell uptake and biological membrane translocation that influence nanomaterial toxicity [6]. In many carbon applications one wishes to decrease contact angle to improve aqueous dispersion [1] or increase biocompatibility [5], but there is also interest in systematically *increasing* contact angle, in particular into the so-called superhydrophobic range beyond 150° to create water-repelling, surface-cleaning surfaces [7]. The technique used most often to increase hydrophilicity (decrease water contact angle) is surface oxidation, where there are a range of competing oxidants and treatment protocols, but very few studies comparing quantitative water contact angles. Recently Mattia et al. [2,8] report enhanced hydrophilicity upon NaOH treatment using CVD films as models for nanotubes and nanopipes. Several recent studies in the nanotube literature use arylsulfonation through diazonium salt chemistry to improve nanotube dispersion [1]. This treatment may extend the range of carbon hydrophilicity, but quantitative comparisons of this and other treatments based on contact angle have not been made to our knowledge.

Much of the recent work on carbon surface chemistry is targeted at nanomaterials, which are difficult and inconvenient subjects for quantitative hydrophilicity characterization. Here we adopt carbon films as model systems for the study of surface chemistry and apply the simple sessile drop technique to compare a variety of chemical surface treatments.

In this study, we fabricate carbon films on quartz slides by physical vapour deposition (PVD), liquid-crystal (LC) spin coating and then carbonization [9], and microwave plasma-enhanced chemical vapor deposition (PECVD); and treat them with a variety of reagents including HNO_3, O_3, NaOH, and sulfanilic acid with sodium nitrite. Most of the experiments are performed on LC-derived films, which are smooth (as-prepared 2.6 nm RMS roughness by AFM) and reveal the effects of surface chemistry independent of the complex effects of roughness. Fig. 1 shows example images of our sessile drops on the various films showing the full range of wetting behavior from 5° to 167° for the equilibrium contact angle. The wetting experiments were done at room temperature in air and quantitative contact angles reported as averages of 2–7 droplets (each 1–5 μL) with the standard error of the mean reported in Table 1.

Table 1 and Fig. 2 summarize the data from this study. The cleaved HOPG (SPI-1 Grade) basal surface and the polyaromatic edge plane of quenched mesophase pitch are similarly hydrophobic with water contact angles near 90°. This suggests that graphene/polyaromatic plane orientation is not a significant factor in carbons if the edge-planes are fully hydrogenated. It further suggests that the low contact angles and large variations in angle seen (5–90° in the smooth films) are primarily due to non-hydrogenated defect sites and heteroatom (O,N,S) functionalization.

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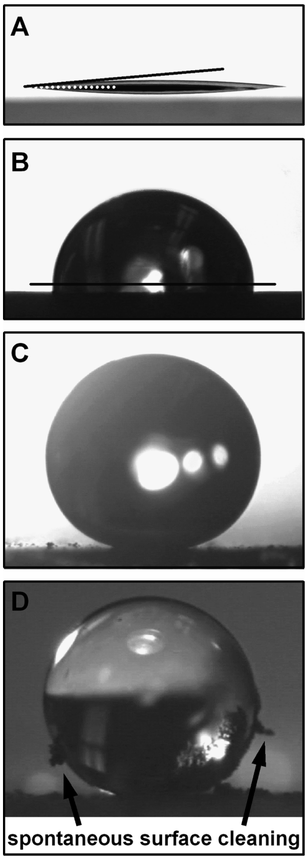
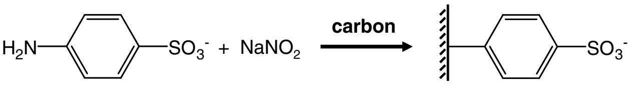


Fig. 1. Example optical micrographs of sessile water drops (typical diameter of near-spherical drops is 1–3 mm) on carbon surfaces employed in this study, using a long-focal-length refracting microscope (Infinity Photo-optical) with fiber optic illumination and CCD video recording. (A) 5° contact angle on PVD carbon films after 5-h aryl-sulfonation at 70 °C; (B) 90° contact angle on freshly cleaved HOPG basal surface; (C,D) 167° contact angle on PECVD carbon films (see Fig. 3). Panel D shows the liquid capture of fine particulate carbon debris spontaneously lifted from the carbon surface illustrating the self-cleaning property of the superhydrophobic PECVD carbon films.

Of the various techniques for surface modification, oxidation is the most common but is limited in effectiveness. The lowest water contact angle achievable with either nitric acid or ozone in this study is 26°. We also find under some conditions that nitric acid treatment can be ineffective (for PVD films) and can even *increase* contact angle (for <3 h treatment of LC-derived films). This increase was unexpected, but was subsequently seen in our laboratory for two other carbon materials. Upon treatment with 10 wt.% nitric acid for 24 h, carbon black (Cabot M120) showed an increase in contact angle from 75° to 96° and supramolecular carbon nanoparticles [10] increased from 83° to 97°, both measured as transient contact angles on pressed pellets. A detailed explanation of this interesting effect is beyond the scope of this letter, but we point out that nitric acid may not only add functional groups, but also destroy or modify existing functional groups and defect-rich disordered carbon, and thus its net effect on the number and hydrophilic strength of surface sites may be complex. Oxidation by ozone (Table 1 and Fig. 2) also showed a dependence on substrate, treatment time (or cycle number) and an apparent hydrophilicity limit of about 26°.

Sodium hydroxide is not widely used to impart hydrophilicity to carbon, but recent reports [2,8] show contact angle reduction from 79° to 44° on a CVD carbon film subjected to 1 M NaOH treatment. NaOH is often used to remove oxidic templates used in nanocarbon synthesis, and this result suggests etching is partially responsible for the reported hydrophilicity of these materials [2,12]. Here we treated PVD carbon films in 1 M NaOH and observe similar contact angle reductions (from 75° to 37–50° depending on temperature and time), which are slowly reversible after water washing (Table 1). This suggests that the NaOH effect is not due to covalent functionalization but to reversible neutralization of surface acid sites and/or formation of surface salt films. The multiple wash cycles in Table 1 may be required to remove surface sodium cations, since some carbon surface oxides are acidic enough to have low proton affinity at neutral pH that makes reverse cation exchange slow.

The most effective hydrophilization treatment demonstrated here uses the sulfanilic acid and sodium nitrite procedure reported by Belmont et al. [13]. Here a carbon film was immersed in 36 mL of sulfanilic acid solution (8.4 mM) at 70 °C. Under continuous stirring 1.5 mL of sodium nitrite solution (0.2 M) was added dropwise and the mixture held at 70 °C for 2 h, followed by six distilled water wash cycles and drying at 100 °C. This route is reported to graft aryl sulfonate groups on carbon (Eq. (1)) through diazonium salt intermediates [1], and is related to the diazonium salt chemistry used in a variety of recent nanotube functionalization schemes [1]. The present method, which generates diazonium salts *in situ* in aqueous solution is particularly easy to perform and achieves contact angles of 5° on both types of carbon films studied here. To our knowledge, this is the lowest contact angle reported to date on smooth carbon surfaces



(1)

This chemistry has two attractive features: (1) it is reported to functionalize the unperturbed graphene basal surface [14], and thus not be restricted to active sites (which in nanotubes comprise tips and sidewall defects), and (2) the grafted sulfonic acid groups are strongly acidic and thus fully anionic and highly hydrophilic over wide ranges of pH. This is in contrast to oxidation processes, which are well known to produce a distribution of surface oxides, many of which are too weakly acidic to be dissociated at neutral pH and thus provide surface polarity rather than the more highly hydrophilic ionic sites. Both features likely contribute to the success of carbon hydrophilization with sulfanilic acid treatment.