Supporting Information

Ice Nucleation Properties of Oxidized Carbon Nanomaterials

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1. Experimental methods

1.1 Preparation of Materials

The preparation of the carboxylated graphene nanoflakes (cx-GNFs) was achieved using an optimized procedure using MWCNTs from Bayer (C150 P) as the starting material.[1] Oxidized MWCNTs (o-MWCNTs) and SWCNTs (o-SWCNTs) were prepared by treatment of MWCNTs and SWCNTs respectively in a 3:1 mixture of conc. sulphuric / conc. nitric acid.[2] Graphene oxide (GO) was prepared using an improved version of the Hummer's method.[3] Mellitic acid was purchased from Sigma-Aldrich and used as received.

1.2 XPS Measurements

XPS measurements for elemental analysis were carried out on a Thermo Scientific K-Alpha XPS machine with a monochromated Al K_α source (E=1486.6 eV). A dual beam flood gun (electrons and argon ions) was used to compensate for charge accumulation on the measured surfaces. All survey scans, shown in Figure S1, were scanned three times with a resolution of 1 eV, 400 μm spot size and 50 ms dwell time.

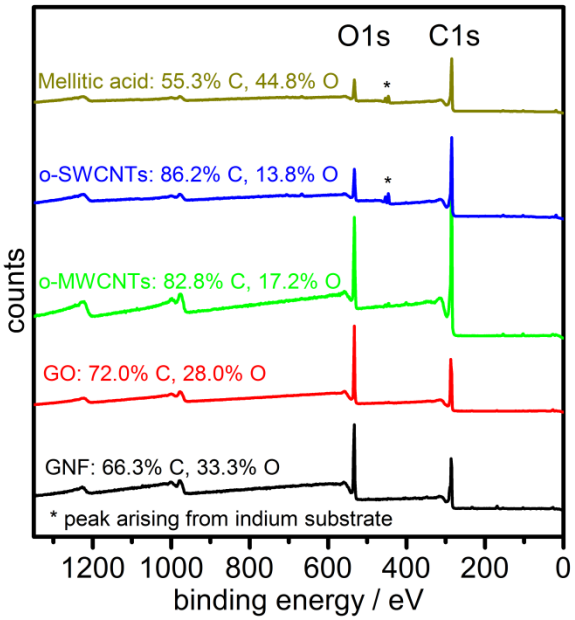

Figure S1 Survey XPS scan of mellitic acid and the carbon nanomaterials tested for ice nucleation activity.

Figure S2 shows high-resolution spectra of the C1s region indicating the presence of C/O functional groups. The spectra were each scanned 10 times with a dwell time of 50 ms and a spot size of 400 microns.

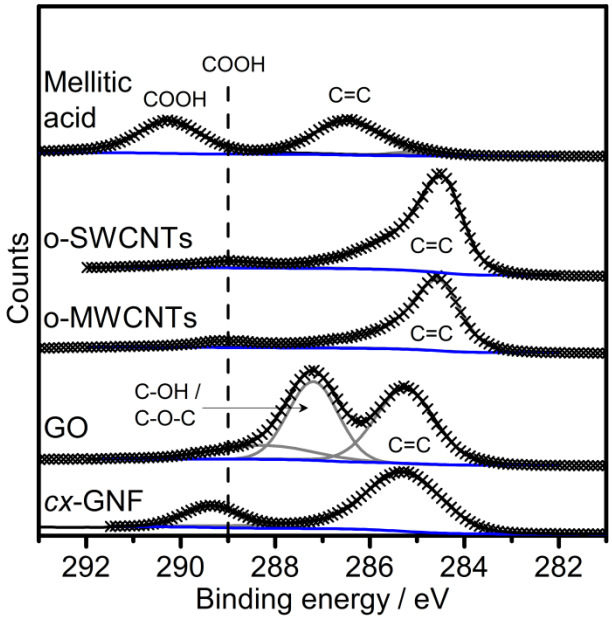

Figure S2 High-resolution XPS spectra in the C1s region. Blue lines are the fitted background and the gray lines are fitted peaks.

1.3 Ice Nucleation Measurements

The µl-NIPI is described in detail by Whale *et al.*[4]. Briefly, 45-55 1 µl droplets are placed on a 0.22 mm thick silanised slide (Hampton Research HR3-231) supported by a Grant-Asymptote EF600 stirling cryocooler using a Picus Biohit electronic micropipette. Suspensions are made up using 18.2 MΩ Milli-Q water and carefully weighed quantities of the nucleant under test. The suspension of O-SWCNTs, which did not disperse completely, was filtered through glass wool prior to use to remove undispersed material. The weight percent of the resulting dispersion was determined by evaporating water from a sample and weighing the remaining mass of material.

The EF600 is used to cool down the droplets at a controlled rate and monitor temperature. In this study a cooling rate of 1°C/min has been used unless otherwise stated. The slide and

droplets are covered by a Perspex chamber with a port for a camera and a gas inlet and outlet. Dry nitrogen is gently flown over the droplets to prevent condensation of water and ice. A camera is used to monitor droplet freezing. Fig. S1 shows the layout of the apparatus. µl-NIPI is used to determine the fraction of droplets frozen at a given temperature. All datasets reported here consist of multiple (2-5) individual experiments. Here we have determined surface site active densities (n_s) values using Equation 1 and also used FROST of Herbert et al[5] to determine the time dependence of ice nucleation by the cx-GNFs.

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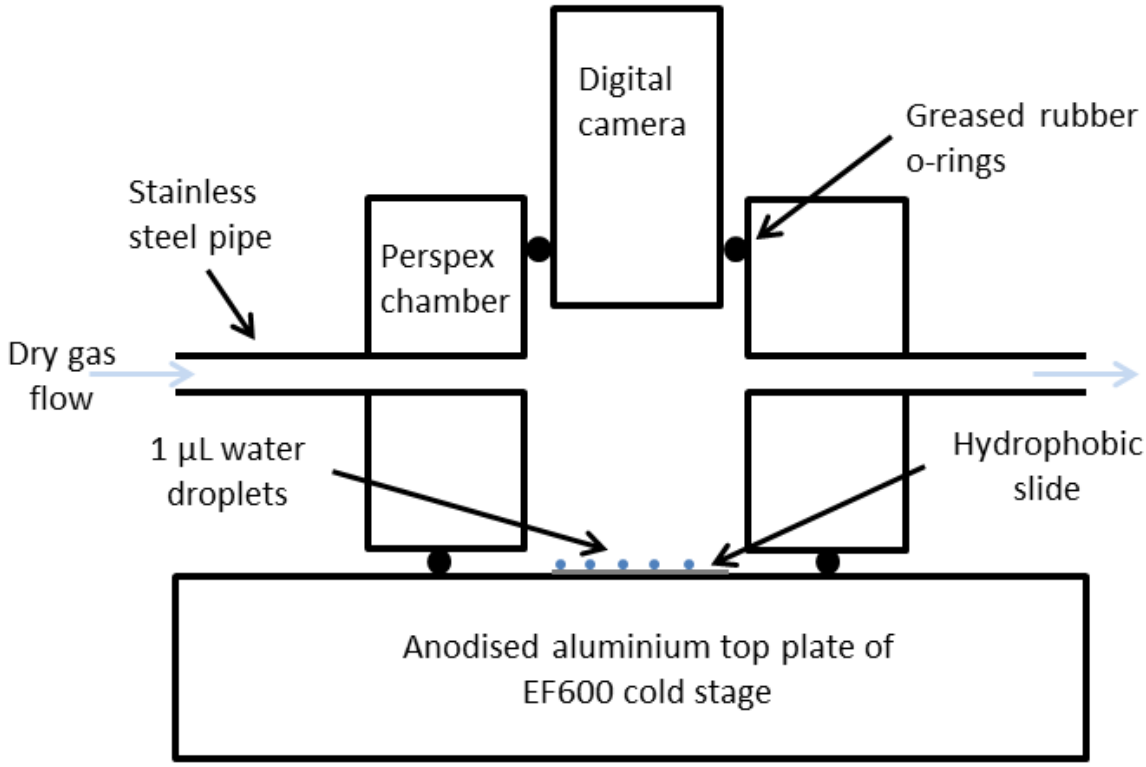

Figure S3 Layout of the µl-NI used PI instrument used in this study. Figure is reproduced from Whale et al[4] under Creative Commons 3.0.

2. Analysis of Time Dependence in Ice Nucleation Data

The *Framework for Reconciling Observable Stochastic Time-dependence* (FROST)[5] describes the cooling rate dependence in droplet freezing experiments which is summarised by the following expression:

$$\Delta T_f = \frac{1}{\lambda} \ln(\frac{r_1}{r_2}) \quad [S1]$$

Where ΔT_f is the change in temperature at a given fraction frozen observed in a droplet freezing experiment upon a change in cooling rate from r_1 to r_2. The systematic shift in cumulative fraction frozen for a change in cooling rate is dependent only on λ, which is an intrinsic property of the nucleant in question. A similar result had been observed experimentally by Vali and Stansbury.[6] The same λ value can also describe the change in the number of droplets expected to freeze in isothermal experiments of varying durations.

Equation 2 can be derived from Equation S1 by choosing a standard cooling rate of 1°C min^{-1}. Modified temperatures can then be calculated for experiments conducted at other ramp rates. As can been seen in Herbert et al[5] multiple experiments conducted at different ramp rates fall onto the same line when normalized using λ demonstrating that this single parameter describes the cooling rate dependence of ice nucleation.

Herbert et al.[5] showed that when a single temperature dependent nucleation rate, $J(T)$, can adequately describe the result of a droplet freezing experiment then ω, the slope of the natural logarithm of freezing rate (or n_s) against temperature,[7] will equal λ. In this case, known as single component stochastic nucleation, nucleation by the particles in each droplet can be described by the same $J(T)$. In contrast, when $\omega < \lambda$ there is particle to particle variability with some particles having a larger $J(T)$. This is termed multiple-component stochastic nucleation and the observed nucleation events will be spread out over a larger temperature range than in the case where each droplet has the same nucleation rate. Hence, observation of ω lower than λ for the same data can be interpreted as evidence for the existence of discrete

nucleating sites on the nucleant, as opposed to a single nucleation rate across the whole surface area of the nucleant.[5, 7] For many nucleating materials it is important to describe the particle-to-particle variability, hence the pragmatic singular description (in the form of n_s) is used which describes the density of active sites, but neglects the time dependence of nucleation.

3. References

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