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# Aggregation Behavior of Detonation Nanodiamond in Solution

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Detonation nanodiamonds (DND) are diamond nanoparticles synthesized through detonation process with 3-5 nm particle size [1]. DNDs are emerging as an important material for a variety of high performance technologies. In particular, their optical and chemical properties, coupled with their lack of cyto-toxicity, make them a preferred candidate for biomedical applications [2]. This includes drug delivery [3], biolabelling [4], and as components of ultra-sensitive contrast agents for magnetic resonance imaging [5]. In each case, however, the realisation of technologies based on their properties is contingent on our ability to control nanodiamonds on an individual and collective basis.

DND has long been believed to show strong tendency to aggregate and form robust superstructures on the order of ~100 nm [5]. Efforts in the purification and dispersion of DND has led to discovery of the existence of discrete DND, mostly based on measurements of light scattering techniques. Theoretical calculations have predicted that such aggregation is due to both coherent (CICI) as well as incoherent (IICI) interfacial columbic interactions [6]. The former interaction should produce ordered configuration whereas the latter random aggregates.

Characterization of nanodiamond aggregates in solution typically relies on the diffraction techniques such as dynamical light scattering (DLS) and small-angle x-ray scattering (SAXS) where particle/aggregate size and shape can be determined. Conventional transmission electron microscopy (TEM) is another commonly applied technique for such purpose, however the specimens have to be dried and not suitable to study the aggregation behavior in solution. Here we use cryo-TEM to directly image the DND particles in solution that are frozen using cryo-plunge freezing method. Detailed atomic and electronic structures of DND were also investigated in combination with FT-IR spectroscopy to form a comprehensive understanding of DND aggregation behavior in solution.

Dedicated cryo-TEM, Krios (Thermofischer) equipped with a direct electron detection camera, K2 (Gatan, Inc) operated at 300kV was used to image the frozen sample of DND in water. High-resolution TEM imaging of the dried sample was carried out using a monochromated, aberration-corrected TEM, Titan (Thermofischer) operated at 80 kV. The low electron beam energy minimizes atomic structural damage.

We unambiguously show that purified DND in water exhibits striking lacey network: a self-assembled rope-like superstructure as shown in Fig. 1a. Our analysis shows that the superstructure morphology has strong particle size and shape dependence. First principles calculations of the particle aggregates suggest that self-assembly is due to the shape and size dependent surface electrostatic potentials of nanodiamond. Further experiments on DNDs from different processing and purifications methods all show similar self-assembly behavior. In addition, HRTEM and EELS confirms that DNDs exhibit distinct diamond cores and fluorine-like shells [7-8], as shown in Fig. 2, regardless the processing method. These observations

further support that the origin of the self-assembly of DND is dominated by non-neutral surface electrostatic interactions.

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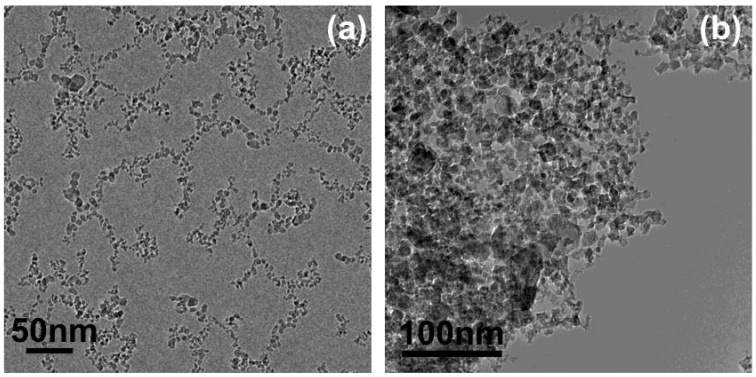


**Figure 1.** (a) Cryo-TEM image of plunge-freezing detonation nanodiamond in water; and (b) BF-TEM image of dried detonation nanodiamond.

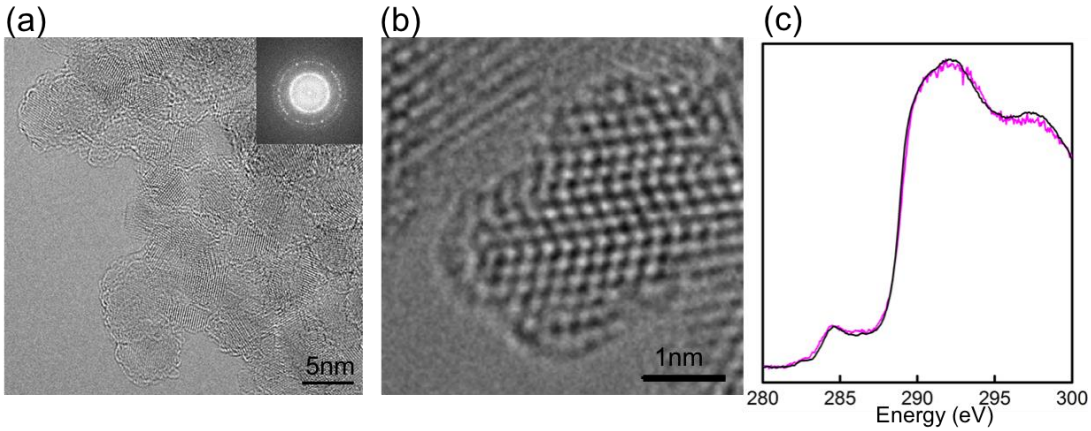


**Figure 2.** Atomic (a-b) and electronic (c) structure of detonation nanodiamond. (a) Typical area of dried detonation nanodiamond, (b) individual nanodiamond showing the structure of diamond core and fullerene-like shell, (c) C-K edge EEL spectra of detonation nanodiamond made with two different purification process, giving positive (black) and negative (pink) zeta potentials.

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