

Surface and Point Defect Measurements of Detonation Nanodiamond using Combined Cs-Cc corrected TEM and *ab initio* Calculations

Shery L. Y. Chang¹, Amanda S. Barnard², Christian Dwyer³, Chris Boothroyd⁴, Eiji Osawa⁵ and Rebecca Nicholls⁶

¹. LeRoy Eyring Center for Solid State Science, Arizona State University, Tempe, USA.

². Virtual Nanoscience Laboratory, CSIRO, Parkville, Australia.

³. Department of Physics, Arizona State University, Tempe, USA.

⁴. Ernst Ruska Center for Microscopy and Spectroscopy with Electrons, Forschungszentrum Juelich, Juelich, Germany.

⁵. NanoCarbon Research Institute, Ueda, Japan.

⁶. Department of Materials, University of Oxford, Oxford, UK.

Detonation nanodiamond (DND), with a particle size typically less than 5 nm, shows great promise in a variety of applications, including drug delivery in biomedical applications [1], and as an agent for biolabelling in fluorescence imaging [2]. More recently, DND has also been identified as a viable candidate for quantum processors [3]. Such applications capitalize on the unusual surface structure and chemistry of DND, as well as the presence of impurities and point defects. Considerable and varied efforts have been made to enhance these unusual properties, including modification of the surface chemistry, and control of the concentration and stability of point defects and impurities. However, due to the small size and complex structure of DND, characterization of its defects and surfaces presents a considerable challenge.

Here we address this challenge by using a state-of-the-art monochromated, spherical- (Cs-) and chromatic- (Cc) aberration-corrected TEM (PICO, FEI Company) to perform quantitative determination of the atomic structure and electronic bonding within DND. The instrument is operated at 80 kV, where the Cs-Cc correction improves the spatial resolution from about 2 Å to the sub-Å level, while this beam energy also has the important benefit of reducing electron beam damage. These benefits are demonstrated by the clearly-visible {311} reflections in the core of the DND particles, as shown in Fig. 1(a). This enables us to quantitatively discern the surface structure of DND, providing an unambiguous experimental evidence of the surface structure. The density-functional tight-binding method [4] has been used to calculate the atomic structure of nanodiamond particles with sizes matching those observed experimentally (Fig. 1(b)). The calculations agree with our observations of fullerene-like surfaces on nanodiamond, and they show that the effect can be interpreted as a type of surface relaxation.

The monochromated TEM used here allows us to perform electron energy-loss spectroscopy (EELS) at an energy resolution of 0.2 eV, enabling us to gain information about the detailed bonding environments of the carbon atoms in DND. Fig. 2(a) shows an EEL spectrum of the DND carbon K-edge, together with reference spectra from bulk diamond and graphite. The interpretation of the near edge structure is guided by simulations of the energy-loss spectra using the density functional method [5]. We have identified a pre-peak in the carbon K-edge that is associated with vacancies in the diamond lattice, as shown in Fig. 2(b). The simulations were also used to quantify the concentration of vacancies in DND. The ability to identify and quantify vacancies in DND is of great importance as it is long believed that vacancies in diamond particles can only exist for particles sizes of tens of nanometers or larger.

Finally, this approach of combined *ab initio* modelling and EELS has also been used to estimate the probability and stability of N-V centers in DND, which is potentially of great importance for the above-mentioned applications.

References:

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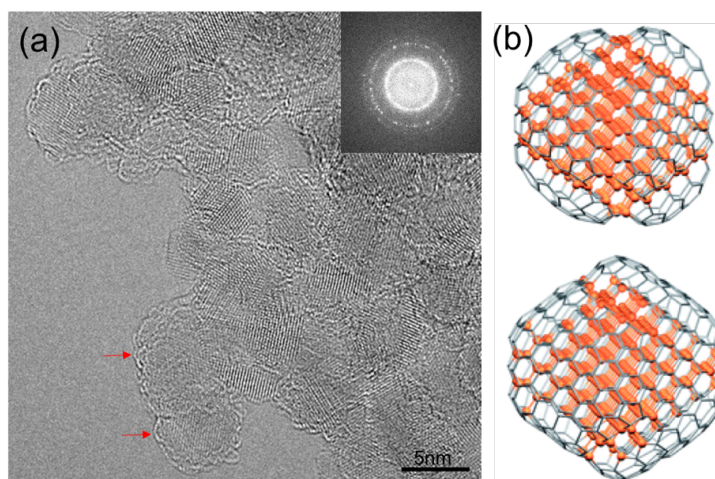


Figure 1. (a) High-resolution TEM image of detonation nanodiamond particles taken using Cs-Cc corrected TEM at 80kV. (b) Atomic structures of nanodiamond particles calculated using DFT tight-binding method. The sp^3 bonds are shown in red and sp^{2+x} bonds are shown in grey.

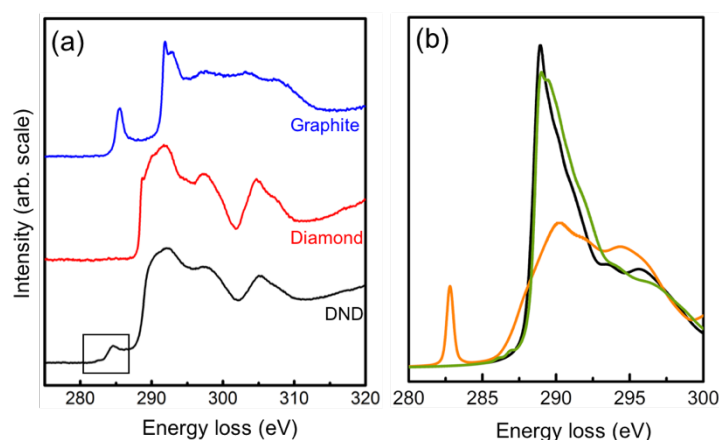


Figure 2. (a) Experimental carbon-K spectra of DND compared to references from bulk diamond and graphite. (b) Simulated K spectra from a carbon atom in pristine diamond (black), a carbon atom nearest to a vacancy (orange), and a carbon atom second-nearest to a vacancy (green). The spectrum from a carbon atom nearest to a vacancy shows a pronounced pre-peak.