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Effects of Surface Chemistry and Crystal Size on Raman Spectra of Nanodiamond

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Detonation nanodiamonds (ND) exhibit exceptional properties due to their small size, rich surface chemistry, and high surface to volume ratio compared to bulk diamonds [1]. These unique characteristics also affect their Raman spectra. While for other carbon nanomaterials Raman spectroscopy is routinely used for analysis of the structure, ordering and dimensions; the presence of large amounts of non-diamond carbon, broad crystal size distributions, and numerous surface functional groups severely limit the potential of Raman spectroscopy for ND characterization due to poor understanding of their spectral features.

We have developed a simple and environmentally-friendly route involving oxidation in air to selectively remove amorphous and sp^2 -bonded carbon from ND [2] and control the average crystal size of the powders [3]. The surface chemistry of the purified ND was controlled by subsequent treatments, e.g. hydrogenation [4]. Using ND powders with different and well-defined surface chemistries, as well as *in situ* Raman measurements at elevated temperatures, we show that the broad asymmetric Raman peaks between 1500 and 1800 cm^{-1} present in all ND powders originate from O-H bending vibrations either from surface functional groups or adsorbed water with contributions (shoulders) coming from sp^2 carbon and C=O stretching vibrations [5].

The Raman spectra of well-purified ND powders can also be used to study the confinement of optical phonons in nanocrystals with the less than 10 nm. The phonon confinement model (PCM) relates changes in the diamond Raman spectrum to the crystal size and can be used for size measurement at the nanoscale. However, crystal size distribution, lattice defects, and the energy dispersion of the phonon modes must be taken into consideration and incorporated into the PCM in order to obtain meaningful data [6].

In summary we have shown that phonon wave vectors from small vibrational domains and surface functional groups (O-H) significantly contribute to the Raman spectrum of ND, giving rise to broad shoulder peaks at $\sim 1250\text{ cm}^{-1}$ and $\sim 1640\text{ cm}^{-1}$, respectively, solving two of the major remaining mysteries in Raman spectroscopy of ND (Fig. 1).

References

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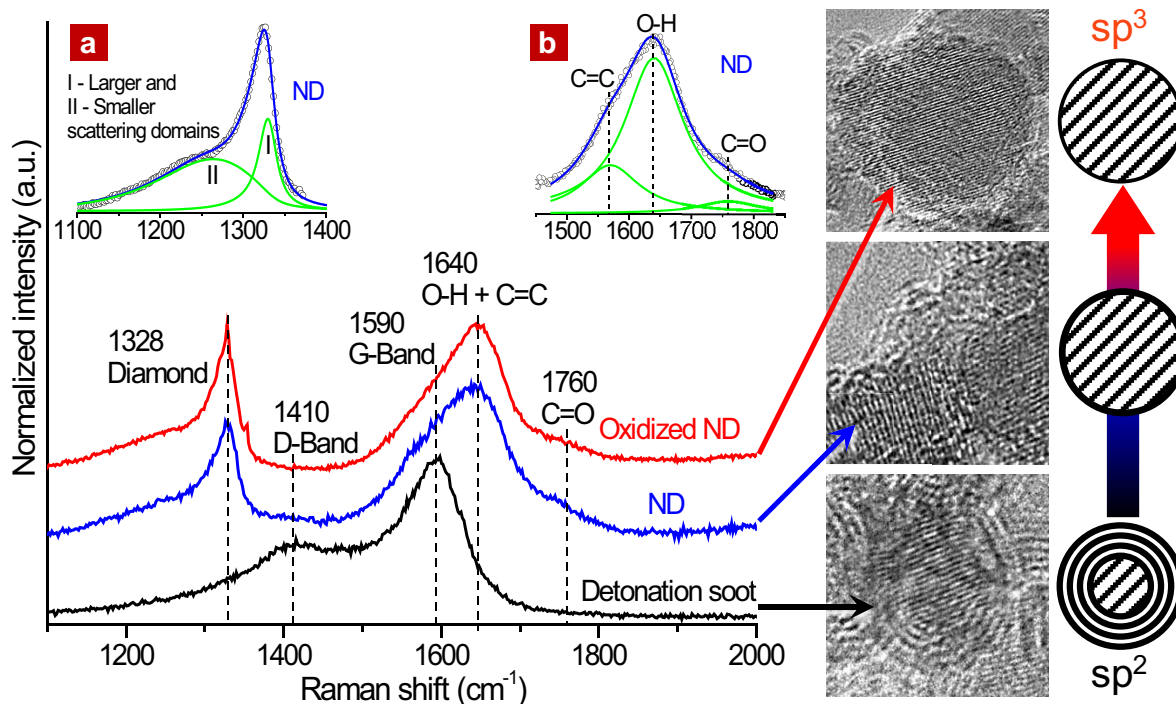


FIG. 1. Electron micrographs showing detonation soot (bottom), purified nanodiamond (middle) and oxidized nanodiamond (top). The diamond cores in detonation soot seem to be completely covered by graphitic shells, and this is confirmed by the Raman spectrum (black line), which is dominated by the G-band of graphitic carbon at 1590 cm^{-1} and has no diamond peak. Purified nanodiamonds are partially covered by a thin layer of graphite, so a diamond peak can be seen at 1328 cm^{-1} in the Raman spectrum (blue line). This thin layer of graphite is completely removed by oxidation in air, so the Raman spectrum of oxidized nanodiamonds has an even stronger diamond peak (red line). The diamond peak in the Raman spectrum of purified and air oxidized nanodiamond (inset **a**) is a combination of peaks originating from larger (I) and smaller (II) coherence scattering domains. The phonon confinement model gives a good fit (blue line) to experimental data (open circles). The broad feature at $1500 - 1800\text{ cm}^{-1}$ in the spectrum of air oxidized nanodiamond (inset **b**) originates from surface functional groups and adsorbed molecules, with some contribution from sp^2 carbon atoms. The Raman spectra were recorded following excitation by an ultraviolet laser (325 nm) (see [1]).

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