X-Ray Spectroscopy of NiO and Nanodiamond at SSRL

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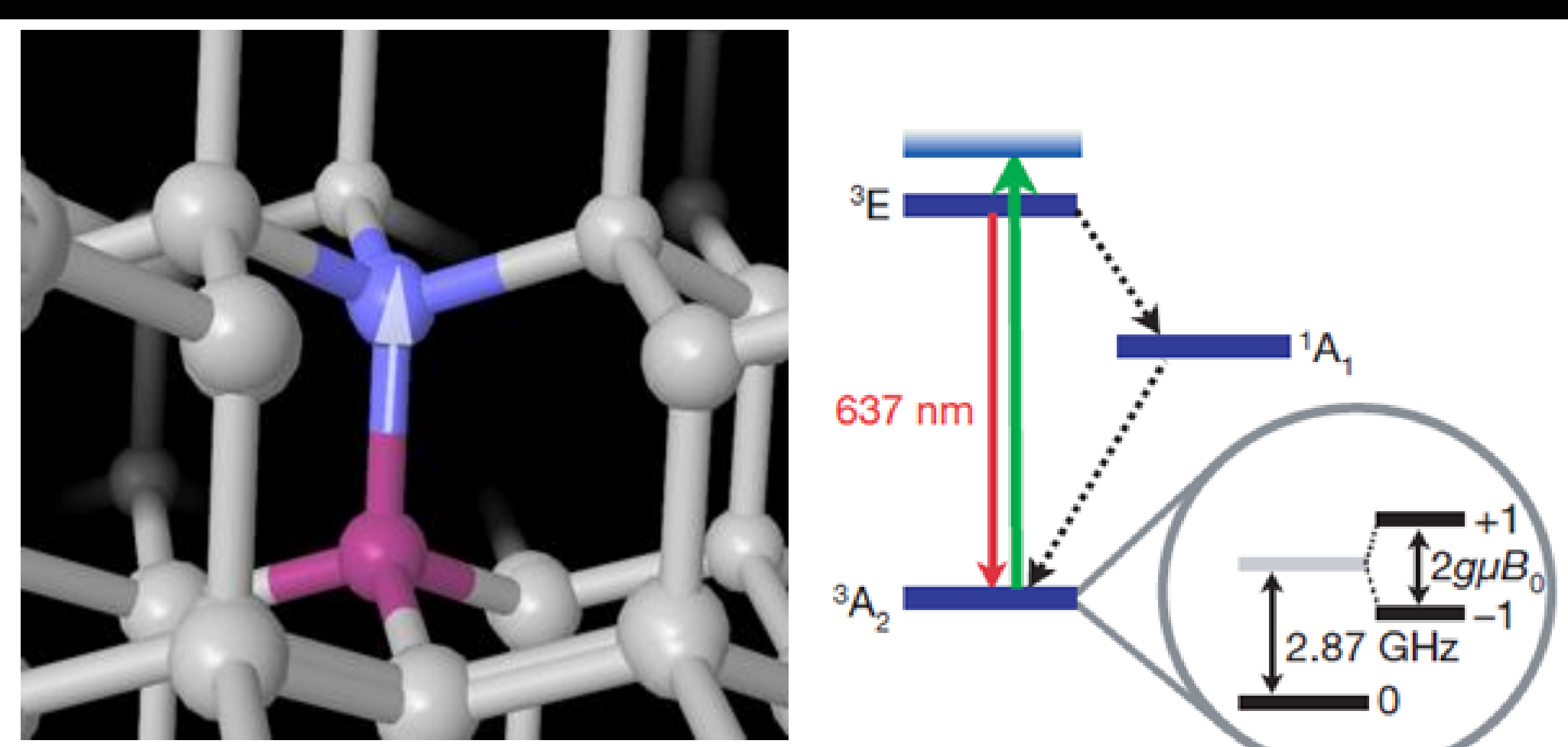
Introduction

XAS is a powerful means of probing the electronic and spatial structures of materials for many fields of scientific research. XAS is a core-level spectroscopy where a photon excites a tightly bound core electron into an unoccupied state. Specifically, in the near-edge region (XANES), the spectra produced offer detailed information about electronic structures. Generating these spectra brings insight into valence, spin-state, orbital symmetry, and other properties of atoms as they interact with one another. X-ray absorption spectra are most often measured via transmission, electron yield (EY) detection and fluorescence yield (FY) detection.

Abstract

The first aspect of this research project focuses on investigating the surface chemistry of high pressure high temperature (HPHT) nanodiamond by using X-ray spectroscopy techniques at the Stanford Synchrotron Radiation Lightsource (SSRL). HPHT nanodiamond is being examined as a biosensing tool for electric field detection based on the fluorescent nitrogen vacancy center hosted within diamond. With use of the transition edge spectrometer (TES), a state-of-the art X-ray fluorescence detector, we are able to probe the surface and bulk properties of diamond. Preliminary work using density functional theory (DFT) has been done, offering insight into ground state energies and electronic structure. DFT will be used to perform future calculations. The second aspect of this research project investigates effects like saturation which distorts the true X-ray fluorescence-yield absorption spectrum, as well as various probing geometries with attention directed towards dilute samples of nickel oxide mixed with graphite. A typical method used to analyze the electronic structure of materials is electron yield detection. However, due to limitations in the escape depth of the electrons in such a method, the overall electron yield spectra is unrepresentative of bulk properties. Thus, we shift techniques to that of florescence yield detection. These two research endeavors serve to improve XAS techniques and advance nanodiamond for medical applications.

Analysis of Nickel Oxide

Spectra of NiO were collected at probing angles of 30°, 55°, and 85°, and at various concentrations (0.1%, 1.0%, 10.0%, and 100%) in graphite. We varied these geometries and concentrations with the intention of properly correcting the distorted spectra. At certain geometries and dilution, peaks become distorted and are less defined. Thus, they are unrepresentative of bulk properties.

Figure 9. Comparison between probing angles 30°, 55°, and 85° of 0.1% NiO concentration and control NiO at 85°. Note the Ni2p$_{3/2}$ multiplet-split peaks at approximately 853.7 eV.

Nitrogen Vacancy Center in ND

Maze et al., Nanoscale magnetic sensing with an individual electronic spin in diamond, **Nature**, 2008

Figure 1-2. Diagram of the nitrogen vacancy center in the nanodiamond lattice (top left) and energy diagram of the nitrogen vacancy center (top right). Individual near-surface nitrogen-vacancy centers (NVC) in the diamond lattice allows for magnetic sensing. Optical pumping to the $m_s = 0$ sublevel of the $^3A_2$ ground state occurs when green excitation of the nitrogen-vacancy center polarizes the electronic spin. Spin-sensitive detection occurs since the rate of fluorescence differs between the $m_s = 0$ and $m_s = \pm 1$ states[2].
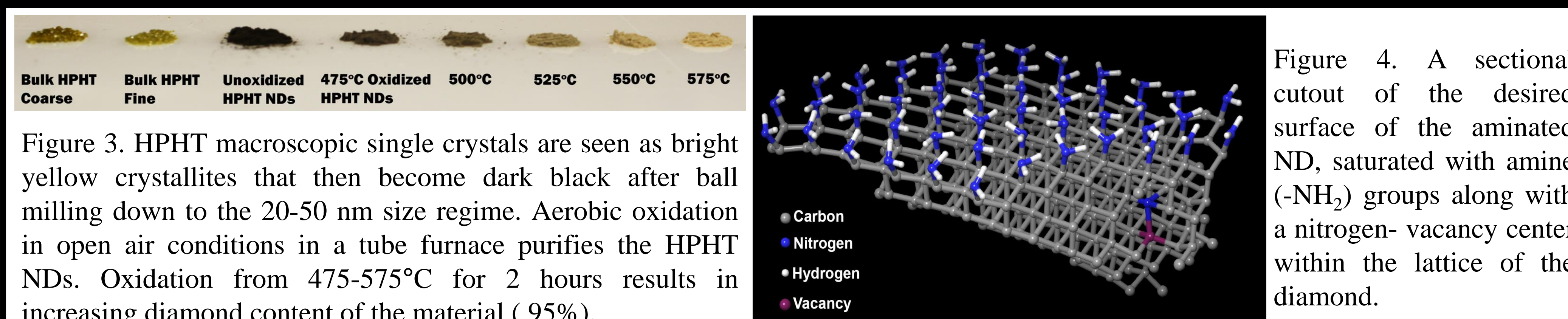
Surface Chemistry of HPHT ND Surface

Figure 3. HPHT macroscopic single crystals are seen as bright yellow crystallites that then become dark black after ball milling down to the 20-50 nm size regime. Aerobic oxidation in open air conditions in a tube furnace purifies the HPHT NDs. Oxidation from 475-575°C for 2 hours results in increasing diamond content of the material (95%).

Figure 4. A sectional cutout of the desired surface of the aminated ND, saturated with amine (-NH$_2$) groups along with a nitrogen- vacancy center within the lattice of the diamond.

- Carbon
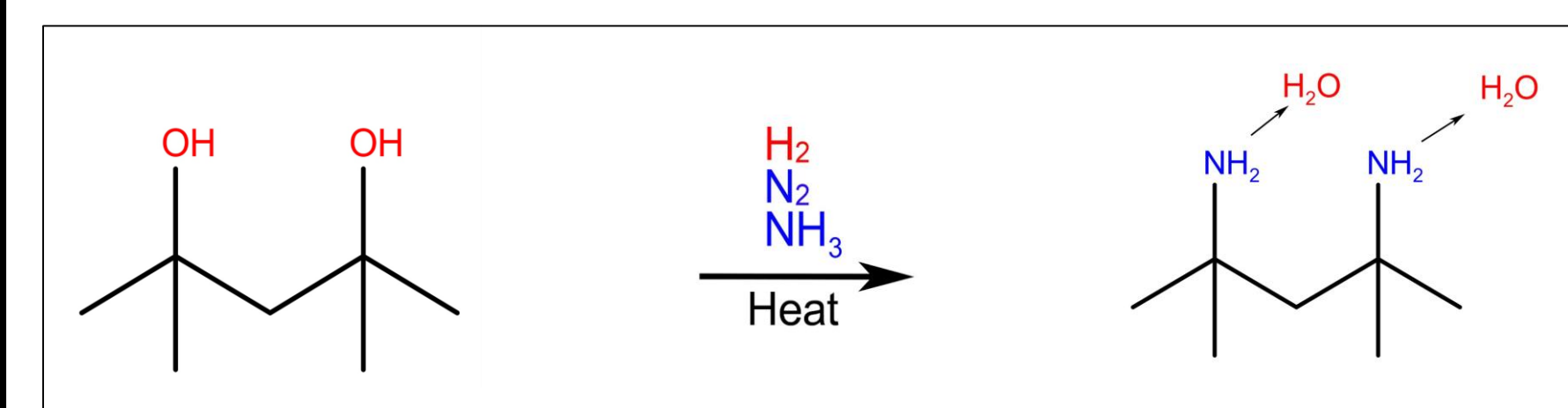- Nitrogen
- Hydrogen
- Vacancy

Figure 5. Proposed general reaction of the ND surface with ammonia to modify the surface of the ND. The ND surface, when oxidized, is saturated with hydroxyl groups and reacted with NH$_3$ gas under high heat to attach an amino group to the α carbon.
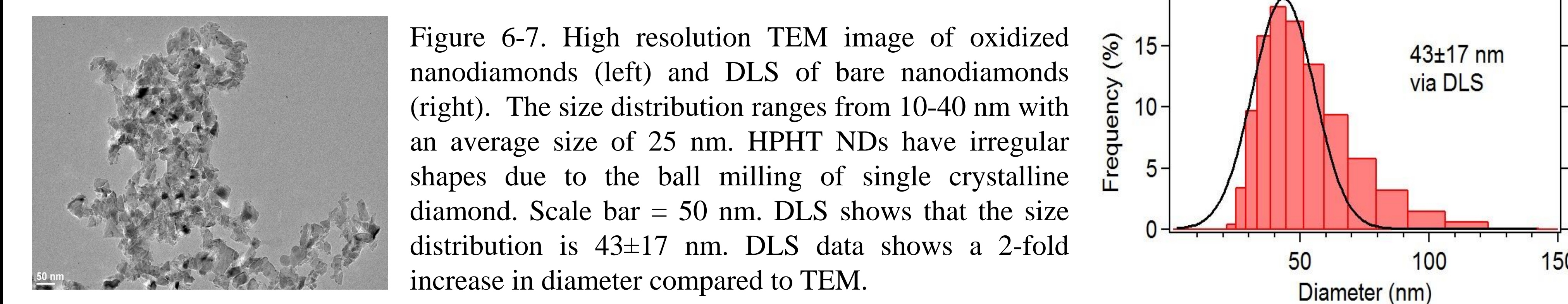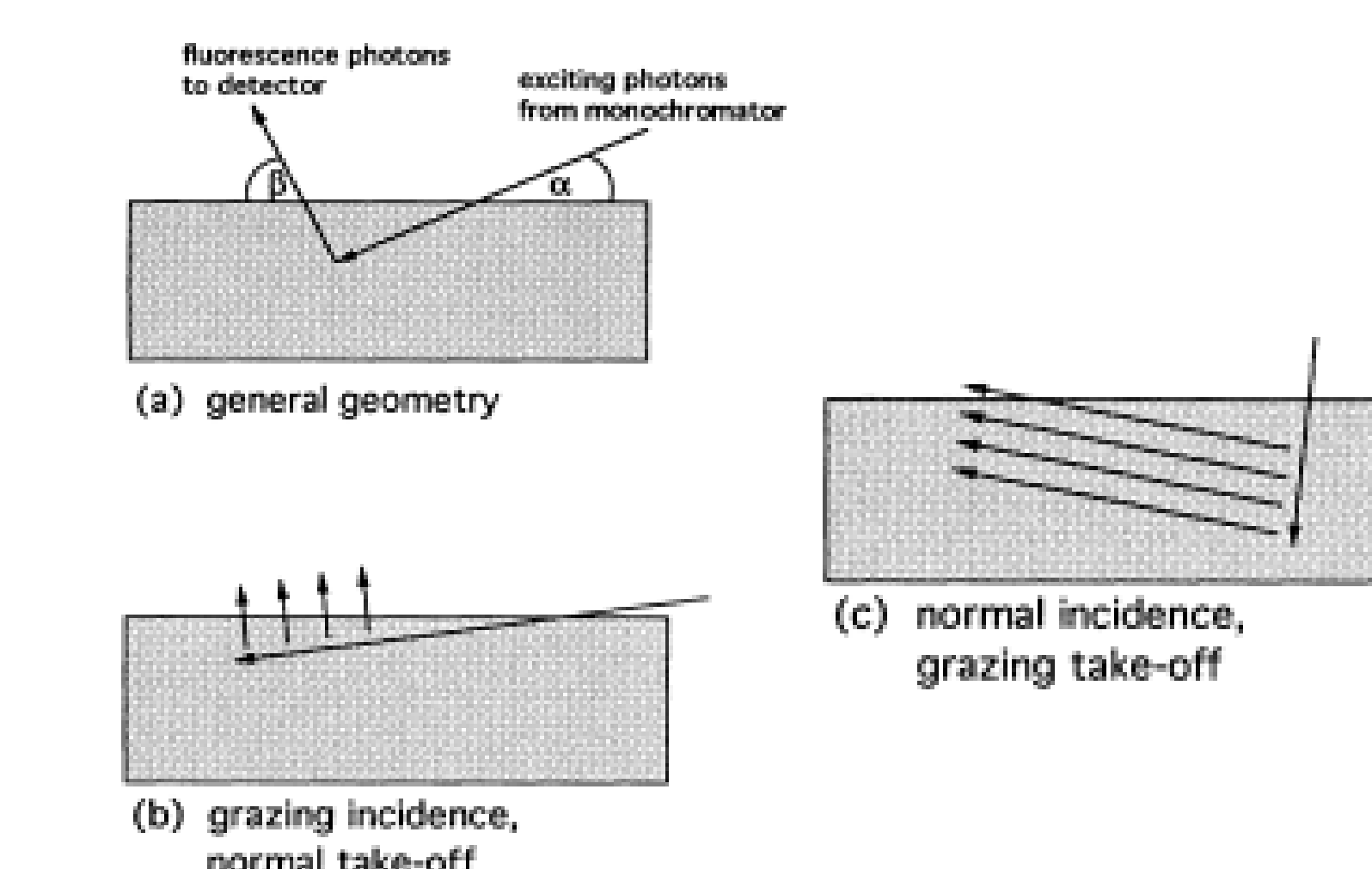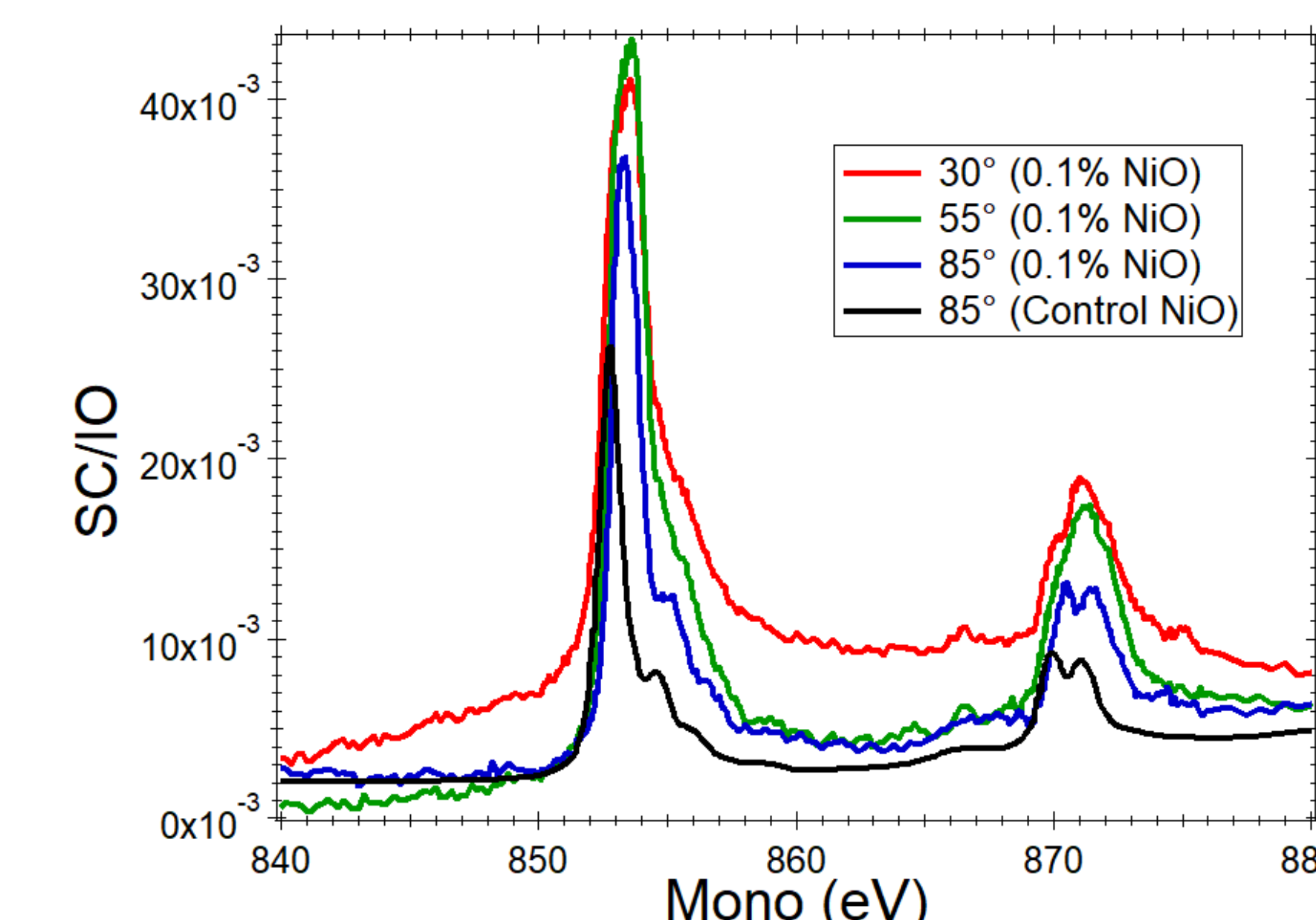

Figure 6-7. High resolution TEM image of oxidized nanodiamonds (left) and DLS of bare nanodiamonds (right). The size distribution ranges from 10-40 nm with an average size of 25 nm. HPHT NDs have irregular shapes due to the ball milling of single crystalline diamond. Scale bar = 50 nm. DLS shows that the size distribution is 43±17 nm. DLS data shows a 2-fold increase in diameter compared to TEM.

43±17 nm via DLS

Future Goals

Regarding nanodiamond, future work would entail using StoBe software to perform density functional theory calculations. More specifically, local density approximations would be generated. These calculations will allow us to compare theoretical results with experimental results, thus potentially verifying to a higher degree, successful aspects of the chemistry. For nickel oxide, the goal is to develop a corrective algorithm in python that accounts for saturation effects, at any dilution of sample and probing angle.

Density Functional Theory

Density functional theory is a computational tool used to describe quantum mechanical systems, in which the primary investigation is of the electronic structure of solid-state matter. Using a functional defined by the spatially dependent electron density, where a functional is merely a function of a function, the properties of a many-electron system can be determined. By treating nuclei of molecules as stationary, a fixed electron state can be described as a wave function $\Psi(\vec{r}_1,...,\vec{r}_N)$ satisfying the many-electron time-independent Schrödinger equation

$$\hat{H}\Psi = \left[\sum_i^N \left(-\frac{\hbar^2}{2m_i}\nabla_i^2 \right) + \sum_i^N V(\vec{r}_i) + \sum_{i<j}^N U(\vec{r}_i,\vec{r}_j) \right] \Psi = E\Psi$$

For the N-electron system, $\hat{H}$ is the Hamiltonian, E is the total energy, and each term represents the kinetic energy, the potential energy from the external field due to positively charged nuclei, the electron–electron interaction energy, respectively.

Saturation Effects , Angle Dependencies, and Dilute Samples

The FY signal, in the case of dilute and thin layered samples, is directly proportional to some coefficient of absorption. For concentrated bulk samples; however, the measured FY is not proportional to the absorption coefficient[1].The shape of the FY spectra is strongly dependent on the sample concentration and measurement geometry. For concentrated samples and grazing incidence measurements, the contrast between the highest and lowest peaks in the spectra will be reduced, leading to a "saturation effect." These distortions in the spectra that are generated vary with each geometry. Hence, the purpose of this investigation. More specifically, they are caused by the absorption of both the exciting photons on their way into the sample and the absorption of the generated fluorescence radiation on its way out of the sample[1]. Figure 8 (right) schematically represents these geometries.

Eisebitt et. al. (1993). Determination of absorption coefficients for concentrated samples by fluorescence detection. Physical review. B, Condensed matter.

Acknowledgements

References

[1] Eisebitt, S & Böske, T & Rubensson, J-E & Eberhardt, Wolfgang. (1993). Determination of absorption coefficients for concentrated samples by fluorescence detection. Physical review. B, Condensed matter. 47. 14103-14109. 10.1103/PhysRevB.47.14103.

[2] Maze, J. R. et al., Nanoscale magnetic sensing with an individual electronic spin in diamond. Nature 455, 644-U41 (2008).