

Introduction

The nitrogen-vacancy center in diamond is a promising tool in oncology, electric field sensing, and quantum cryptography. High-pressure high-temperature (HPHT) nanodiamonds (NDs) are prime contenders for these fields because they host nitrogen-vacancy centers (NVCs) which are applicable towards cancer detection and electric and magnetic field sensing. However, to apply HPHT NDs to these fields, the surface must first be functionalized—a difficult process because of the inert nature of the surface. The project at hand focuses on surface modification of HPHT NDs with amines to allow for further bioconjugation of small molecules and plasmonic shells. This is done via liquid-phase chemistry and high-temperature gas-phase chemistry. To characterize the surface of aminated NDs, samples are probed using synchrotron radiation at the Stanford Synchrotron Radiation Lightsource (SSRL) alongside the transmission edge spectroscopy (TES) detector. With verification of a homogeneously amine-terminated surface, the NDs are prepared for further functionalization which can be targeted to enhance the properties of the NVC charge states for applications in enhanced electric field and voltage sensing.

Fluorescent HPHT NDs

HPHT NDs gain their fluorescent properties from nitrogen-vacancy centers—a defect that occurs when a nitrogen atom displaces a carbon atom, resulting in an adjacent vacancy in the diamond lattice. To enhance the properties of the NVC charge states, NV⁰ and NV⁻, HPHT NDs are functionalized with amines (-NH₂) to allow application in fields such as quantum cryptography and voltage sensing.

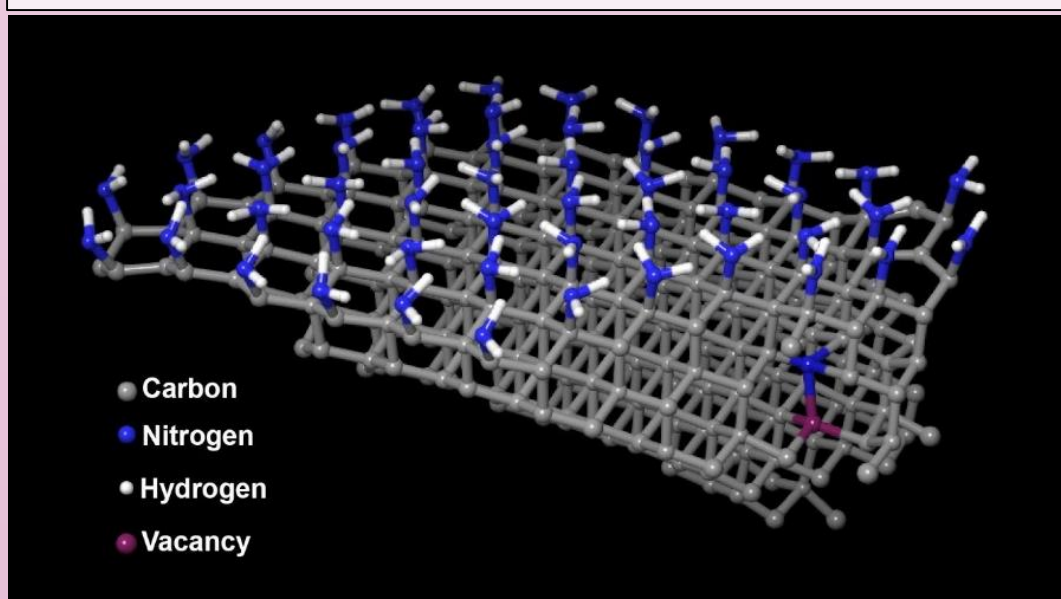


Figure 1. A cross-sectional view of the desired amine-terminated surface of HPHT NDs featuring a nitrogen vacancy center within the structure of the diamond.

Surface Modification of Inert NDs

The surface of NDs is inert, therefore making it impossible to modify directly. However, due to natural surface impurities such as carbonyl groups, it is possible to modify their surface by heating to high temperatures within a tube furnace. HPHT NDs undergo oxidation when heated to 550°C, resulting in a homogeneous hydroxyl (-OH) terminated surface is created to act as a precursor to further chemistry.



Figure 2-3. HPHT nanodiamonds in boats prior to oxidation (left) and after nearly 24 hours of oxidation at 550°C (right). A light tan color is sign of well-oxidized nanodiamonds.

Activation of ND Surface

Oxidized NDs are alcohol rich, but they have limited reactivity towards direct amination. To activate the ND surface, thionyl bromide (SOBr₂) is used to convert the hydroxyl groups into bromine groups. These groups are essential to amination as they are highly reactive and act as a strong leaving group during the amination process. This is done to maximize the amination levels.

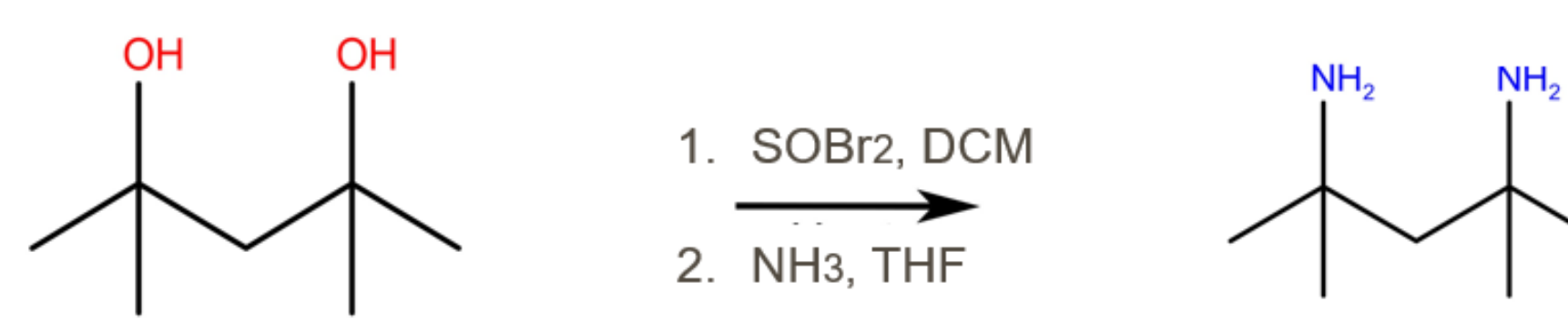


Figure 4. Mechanism for bromination of oxidized diamonds and subsequent amination of brominated diamonds.

Amine Functionalization of HPHT NDs

Wet Chemical Modification

Liquid amination is achieved by combining an ammonia-THF solution with brominated nanodiamonds in air-free conditions. The reaction is allowed to stir for 2 hours on a dry Schlenk line. Upon completion of the reaction, aminated NDs are ready for washing and purification via centrifugation on a high-speed centrifuge.



Figure 4. Vials of two samples of nanodiamonds undergoing liquid amination.

High Temperature Gaseous Amination

Gas-phase amination chemistry is completed using a tube furnace capable of controlling gas temperature and pressure. Ammonia gas (NH₃) is allowed to run for 2 hours, where samples are heated between 200°C and 700°C in an oxygen-free environment.

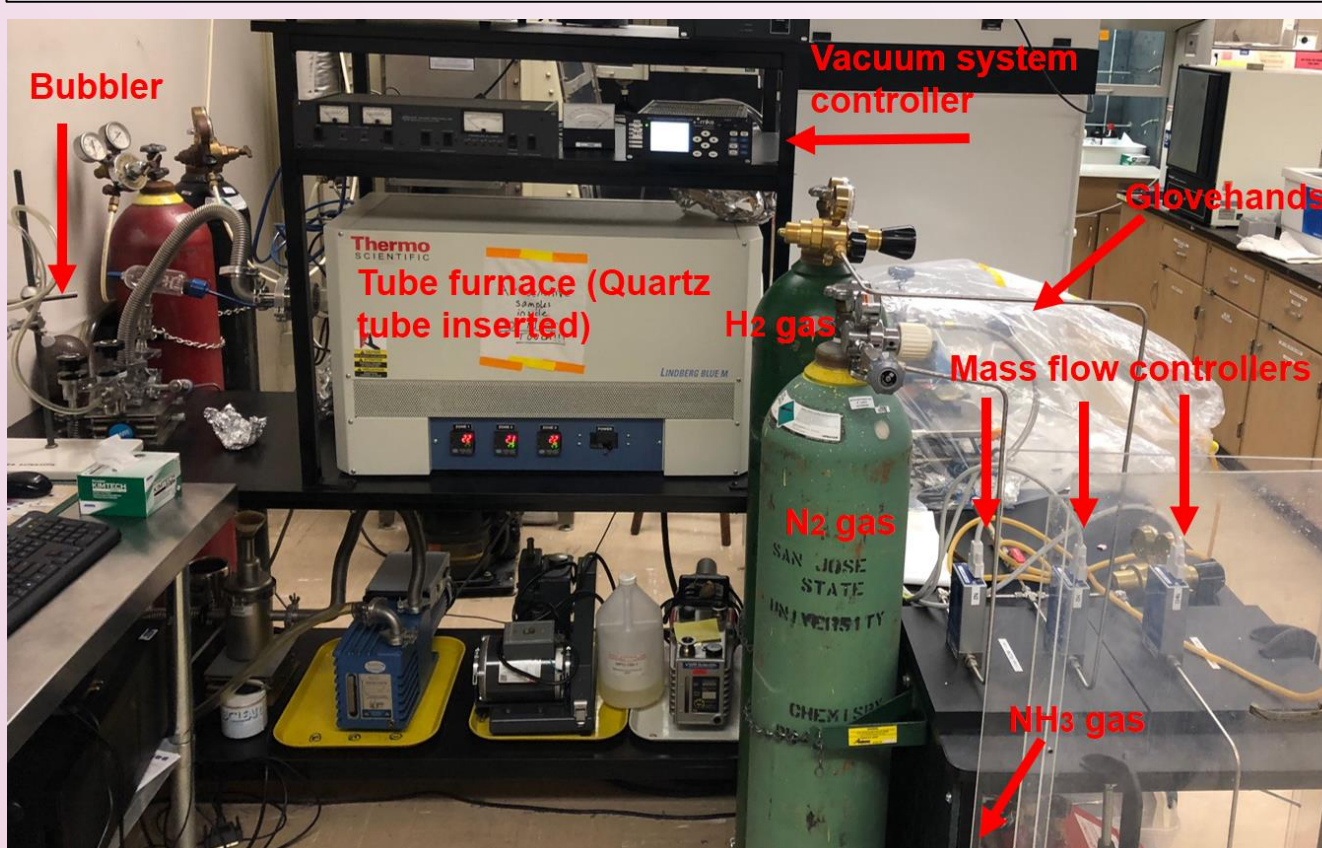


Figure 5. Tube furnace with vacuum apparatus below. It is capable of heating up to 1100 °C and achieving vacuums as low as 10⁻⁵ torr. N₂, H₂, and NH₃ flows are controlled by the vacuum system controller which regulates mass flow controllers. The flow of gas travels from the gas tanks, through the quartz tube, into the bubbler, and into a fume hood.

Condensation of NH₃ for Low-Temperature Amination

Condensation of NH₃ occurs by allowing NH₃ gas to flow through a dry Schlenk line and into the ND sample flask, which is cooled in a dry ice and isopropanol solution. This achieves temperatures below the boiling point of NH₃, resulting in condensation of NH₃. Once a sufficient amount of NH₃ condenses in the reaction flask, the sample is allowed to react and stir for two hours. Subsequent workup requires resulting NH₃ to evaporate from flask.



Figure 6. NH₃ condensing in reaction flask containing NDs and stir bar.

X-Ray Absorption Findings

X-ray absorption spectroscopy (XAS) and X-ray photoelectric spectroscopy (XPS) at Stanford Synchrotron Radiation Lightsource (SSRL) is used to probe the surface chemistry on samples of aminated NDs. This is done on beamlines 8-2 and 10-1 under supervision by SSRL material scientist Dennis Nordlund and graduate student Jamie Titus. Results indicate the presence of various nitrogen moieties, ranging from imides (C=N) at 400eV to amines (C-NH₂), whose C-N bond resonates at approximately 405eV, and N-H bonds resonate at approximately 401eV.

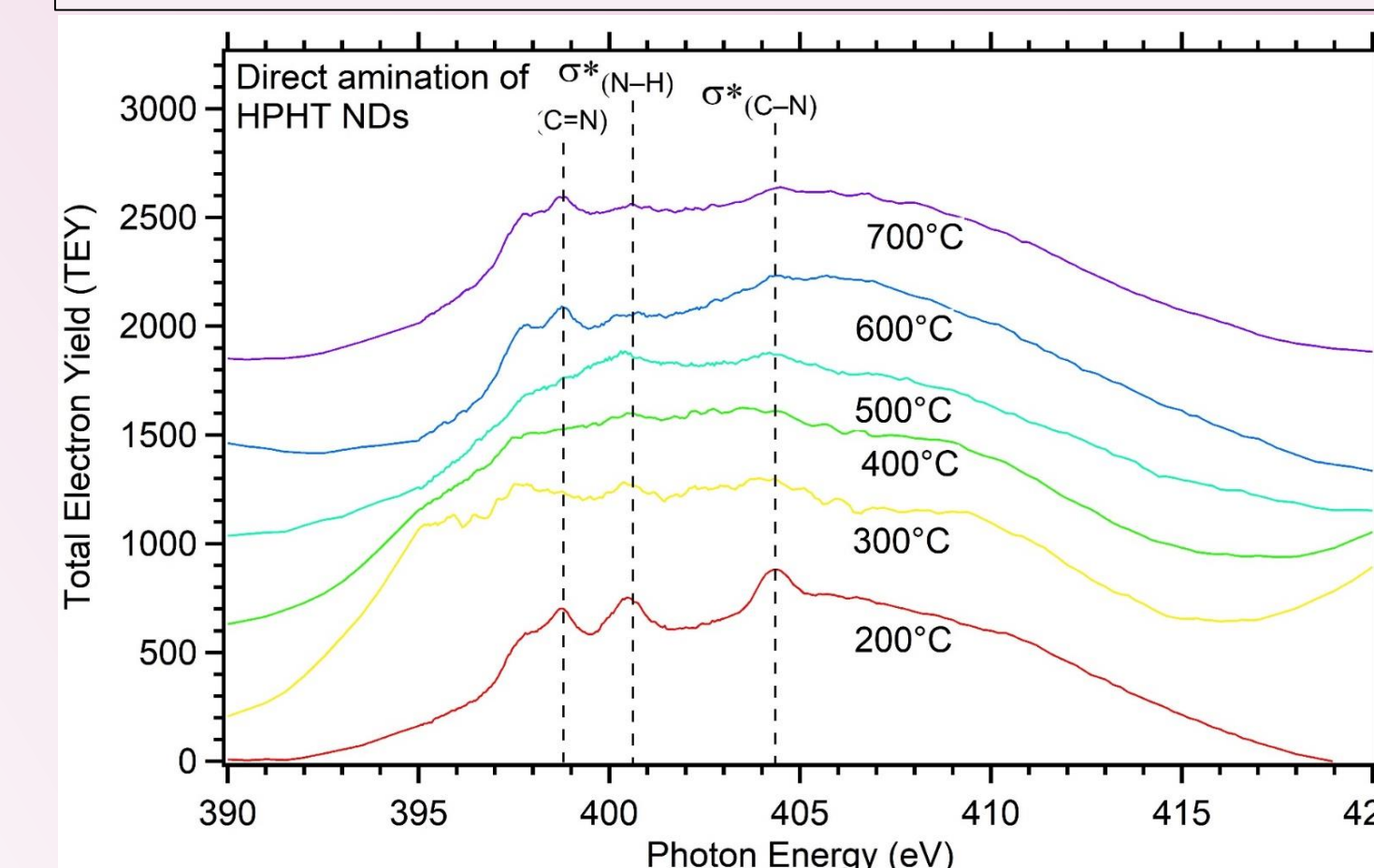


Figure 7. Data accumulated from SSRL in December 2017. Samples include those aminated in the tube furnace from 200 °C to 700 °C.

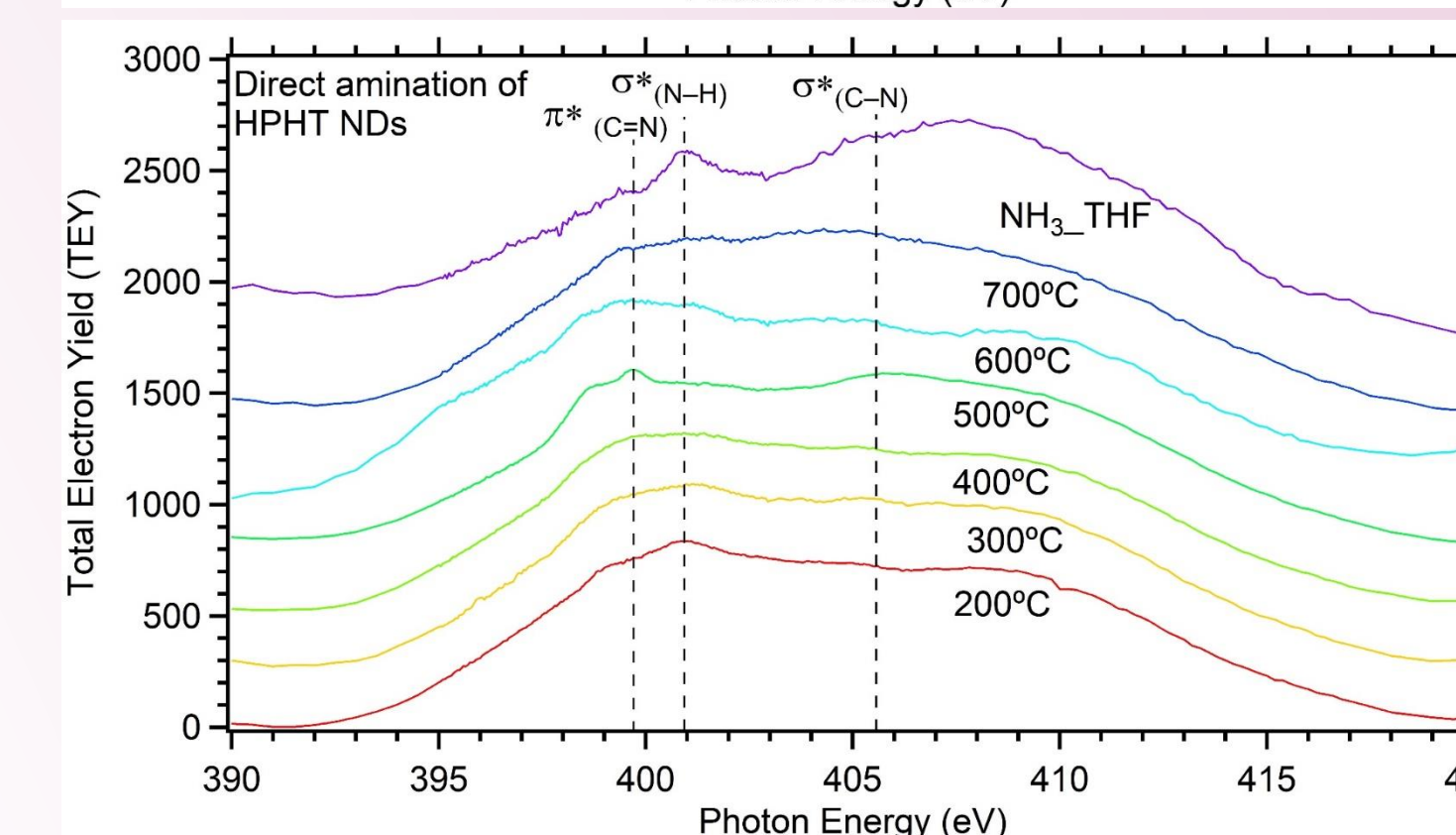


Figure 8. Data accumulated from SSRL in June 2018. Samples include those aminated in the tube furnace from 200 °C to 700 °C and a sample aminated using liquid NH₃.

Future Steps

XAS and XPS results indicate strong signals of nitrogen groups (C=N, C-N, and N-H). Having achieved successful levels of amination, density functional theory (DFT) calculations will be done to predict the electronic structure of nitrogen. Aminated NDs will undergo functionalization with polyethylene glycol (PEG) and bioconjugation of small molecules and plasmonic shells. Further work will also be done to enhance NVC fluorescence.

Acknowledgements

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