

# Wednesday Morning, October 21, 2015

## Nanometer-scale Science and Technology

Room: 212B - Session NS-WeM

### Nanodiamond for Optical and Biomedical Applications

**Moderator:** Huan-Cheng Chang, Academia Sinica, Olga Shenderova, Adámas Nanotechnologies Inc.

#### 8:20am NS-WeM2 Time-Resolved Luminescence Nanothermometry with Nitrogen-Vacancy Centers in Nanodiamonds, *O.C. Chen, Pei-Chang Tsai*, Academia Sinica, Taiwan, Republic of China

We have developed FNDs into a nanoscale luminescence thermometer for both temporally and spatially resolved temperature sensing with hosted NV<sup>-</sup> centers, time-resolved luminescence nanothermometry was demonstrated with 100-nm FNDs spin-coated on a glass substrate and submerged in gold nanorod solution heated by a near-infrared laser, a pump-probe-type experiment that enables the study of nanoscale heat transfer with a temporal resolution of better than 10  $\mu$ s. Moreover, we present a three-point sampling method that allows real-time monitoring of the temperature changes over  $\pm 100$  K, an advantage of this three-point method is that it possesses a built-in ability for self-correction of signal fluctuation. To verify the validity of these measurements and to understand the heat transfer in the nanometer and microsecond scales, we carried out heat transfer numerical simulations. The simulated time constants for single exponential decays are  $\tau = 20$   $\mu$ s at  $r = 1.0$   $\mu$ m and  $\tau = 25$   $\mu$ s at  $r = 1.5$   $\mu$ m, compared with our experimental observations of 12 and 18  $\mu$ s, respectively. Finally, the present study represents the first demonstration of thermometric investigation at the nanometric length scale with microsecond time resolution. It adds an important new dimension to the use of NV<sup>-</sup> centers in diamond for quantum sensing applications.

Reference:

(1) Toyli, D. M.; Christle, D. J.; Alkauskas, A.; Buckley, B. B.; Van de Walle, C. G.; Awschalom, D. D. Measurement and control of single nitrogen-vacancy center spins above 600 K. *Phys. Rev. X* **2012**, 2, 031001.

(2) Loza, P.; Kouznetsov, D.; Ortega, R. Temperature distribution in a uniform medium heated by linear absorption of a Gaussian light beam. *Appl. Opt.* **1994**, 33, 3831–3836.

#### 8:40am NS-WeM3 Nanoscale Measurement and Diagnostics using Diamond Quantum Probes, *Jörg Wrachtrup*, Universit of Stuttgart, Germany **INVITED**

Diamond defects are a novel class of nanoscale quantum sensors. They are capable of measuring forces, pressure, temperature, magnetic and electric field with high accuracy on length scales of a few nano meters. The nano sensors function under various environmental parameters including ambient conditions. Diamond defect can be either enclosed in nanocrystals 1D or 2D materials depending on the application purpose. The talk will highlight various applications comprising precision measurement of magnetic, electric field and pressure with application in energy management systems and bioimaging.

#### 9:20am NS-WeM5 Measurement of Carbon Condensates Using Small-Angle X-ray Scattering During Detonation of High Explosives, *Trevor Willey, M. Bagge-Hansen, L.M. Lauderbach, R. Hodgins, S. Bastea, L. Fried, A. Jones, D. Hansen, J. Benterou, C. May*, Lawrence Livermore National Laboratory, *T. Graber*, Washington State University, *B.J. Jensen, D. Dattelbaum, R. Gustavsen, E. Watkins, M. Firestone*, Los Alamos National Laboratory, *J. Ilavsky*, Argonne National Laboratory, *T. van Buuren*, Lawrence Livermore National Laboratory

Detonation is one of the primary methods to produce nanodiamond. A new small-angle x-ray scattering (SAXS) end station has been developed by LLNL for use at the new Dynamic Compression Sector at the Advanced Photon Source to observe carbon condensation during detonation of high explosives. The beamline and endstation are capable of synchronously initiating detonation and then acquiring up to four SAXS patterns from single x-ray pulses, which in 24-bunch mode at the APS are < 100 ps and arrive every 153.4 ns. Timescales are ideal: detonation investigation and model validation requires data regarding processes occurring at nanometer length scales on time scales ranging from nanoseconds to microseconds. The endstation and beamline have now demonstrated unprecedented fidelity in SAXS data during detonation; for the first time the data contains a clear Guinier knee and high-fidelity power law slope, giving information about the size and morphology of the resultant nanoparticles. We have commenced investigating HNS which is an explosive known to produce copious graphitic soots, RDX/TNT mixtures similar to what is commonly

used to produce nanodiamond, and DNTF, a hydrogen-free, nitrogen rich, hot, and high velocity explosive. HNS produces carbon particles with a radius of gyration of 3 nm in less than 400 ns after the detonation front has passed, and this size is constant over the next several microseconds. The power-law slope is about -3, consistent with a disordered, irregular, or folded sp<sup>2</sup> structure. Comp B, a 60% RDX, 40% TNT mixture, produces 3 nm particles also within a few hundred ns, and has a power law that is around -3.7, consistent with 3D nanodiamond particles. DNTF produces larger, 7 nm particles with a power law that is -4 over the first few hundred ns and then decreases to -3.8, ultimately also consistent with 3D diamond nanoparticles. In all three cases, particles are produced in the first few hundred ns, and then do not appreciably grow over the next several microseconds, which is in direct contradiction to previous pioneering work on RDX/TNT mixtures, TATB, and several other explosives, where observations indicate significant particle growth (50% or more) continues over several microseconds.

#### 9:40am NS-WeM6 Surface Functionalization of Nanocarbons Formed from Detonating High Explosives, *Bryan Ringstrand, R.C. Huber, D. Podlesak, D. Dattelbaum, R. Gustavsen, M. Firestone*, Los Alamos National Laboratory

High explosive detonation is an exothermic process where CHNO molecules are transformed into, but not limited to, H<sub>2</sub>O, CO, CO<sub>2</sub>, N<sub>2</sub>, and solid carbon (i.e. soot). The type and quantity of carbon allotrope present depends on the explosive formulation and the temperature and pressure of the detonation. The carbon allotropes that form during a detonation include nanodiamond, graphite, and amorphous carbon; however, nanodiamonds are the most interesting. Due to their chemical inertness and biocompatibility, nanodiamonds have garnered interest in biomedical and electronic applications.<sup>1</sup>

The nature of a detonation event produces soot that is contaminated with metals, metal oxides, and other carbon phases (i.e. sp<sup>2</sup> carbons). Removal of these species is essential to obtaining pristine nanodiamond. Metals and metal oxides are removed using mineral acid treatments; whereas, sp<sup>2</sup> species are thermally oxidized above 400 °C.<sup>2</sup> Although acid treatment and thermal oxidation generate pristine nanodiamond, these methods damage the characteristic markers that provide information about the processes and conditions that give rise to nanodiamond as a carbon allotrope.

Another benign approach could be surface functionalization of the soot followed by separation of functionalized and non-functionalized components. Carbon nanotubes have been known to de-aggregate and disperse in ionic liquids.<sup>3</sup> A similar approach was demonstrated for pristine nanodiamond using an imidazolium based ionic liquid covalently bound to its surface. These functionalized nanodiamonds showed increased dispersibility in polar solvents and formed stable gels in other ionic liquids.<sup>4</sup>

Our efforts to adapt ionic liquids for the surface functionalization of nanocarbons produced by high explosive detonation will be discussed. Specifically, imidazolium based ionic liquids incorporating decyl chains through various coupling strategies will be reviewed. The functionalized nanocarbons could then be dispersed in solvents, allowing for individual component isolation and size fractionation. The isolated products were characterized using a range of techniques including SEM, TEM, powder X-ray diffraction, X-ray scattering, and XPS.

References:

1. Krueger, A.; Lang, D. *Adv. Funct. Mater.* **2012**, 22, 890.
2. Pichot, V.; Comet, M.; Fousoon, E.; Baras, C.; Senger, A.; Le Normand, F.; Spitzer, D. *Diam. Relat. Mater.* **2008**, 17, 13.
3. Fukushima, T.; Kosaka, A.; Ishimura, Y.; Yamamoto, T.; Takigawa, T.; Ishii, N.; Aida, T. *Science* **2003**, 300, 2072.
4. Park, C.; Young, A. Y.; Lee, M.; Lee, S. *Chem. Commun.* **2009**, 5576.

#### 11:00am NS-WeM10 Quantum Sensing in Biology using the Nitrogen-Vacancy Centre in Diamond, *L.J. Hollenberg, David Simpson*, University of Melbourne, Australia **INVITED**

The nitrogen-vacancy (NV) defect centre in diamond can be used as a single spin quantum probe for nanoscale magnetometry. Optically, it possesses a broad absorption band from 512-560 nm, sustained fluorescence from 630-750 nm, is chemically inert and bio-compatible, making it ideal for room-temperature applications. The populations in the spin-1 sublevels of the NV ground state, which are sensitive to local magnetic fields, can be measured and polarised optically, and controlled via resonant microwave fields (~ 3 GHz). Through various quantum control schemes the NV centre has been used to detect static (DC), sinusoidal (AC) and fluctuating (FC) magnetic fields. This talk will briefly review some of the overall progress and applications of the NV centre in the detection of electronic and nuclear

spins at the nanoscale, including our own work on the quantum measurement of nanodiamond-NV centres in a living cell, detection of Gd spin labels in a lipid bi-layer, and T1-based electron spin resonance techniques for the non-invasive detection of magnetic species.

11:40am **NS-WeM12 Large Scale Production of Fluorescent Nanodiamond Particles**, *Olga Shenderova, N.J. Nunn, G.E. McGuire*, Adámas Nanotechnologies Inc.

Nanodiamond (ND) particles have recently emerged as a key platform for many sectors of nanoscience and nanotechnology due to their outstanding mechanical performance, biocompatibility and distinctive optical properties, a combination of assets not often met in the nanoworld. Particularly production of ND particles containing nitrogen-vacancy (NV) color centers exhibiting stable luminescence and unique spin properties have brought ND particles to the forefront of materials research. Based on the SBIR award from National Institute of Health (NIH), Adámas Nanotechnologies developed a large scale production of ND containing NV color centers in hundreds of grams batches. While nitrogen is an intrinsic impurity in diamond, vacancies must be created by high energy irradiation. Variety of factors play a role in creation of a high density ensemble of NV centers in NDs including density of substitutional nitrogen, size of starting particles that undergo irradiation, irradiation dose and temperature, post irradiation processing including fragmentation to the smaller sizes. In the paper, role of these factors will be discussed. Production of fractions of NDs with median sizes ranging between 10 and 100 nm was demonstrated, exceeding by an order of magnitude brightness of a relevant typically used organic dye for NDs with sizes exceeding 50nm. The brightness of fluorescent nanodiamonds and an organic dye was compared side-by-side under identical conditions using total internal reflection fluorescence microscopy (TIRFM) measurements at NIH.

Acknowledgment: Contract HHSN268201300030C, NHLBI COAC Services Branch RFP No. PHS 2013-1, Topic 80, "Fluorescent Nanodiamonds for In Vitro and In Vivo Biological Imaging"

# Authors Index

**Bold page numbers indicate the presenter**

## — B —

Bagge-Hansen, M.: NS-WeM5, 1  
Bastea, S.: NS-WeM5, 1  
Benterou, J.: NS-WeM5, 1

## — C —

Chen, O.C.: NS-WeM2, 1

## — D —

Dattelbaum, D.: NS-WeM5, 1; NS-WeM6, 1

## — F —

Firestone, M.: NS-WeM5, 1; NS-WeM6, 1  
Fried, L.: NS-WeM5, 1

## — G —

Graber, T.: NS-WeM5, 1  
Gustavsen, R.: NS-WeM5, 1; NS-WeM6, 1

## — H —

Hansen, D.: NS-WeM5, 1

Hodgin, R.: NS-WeM5, 1

Hollenberg, L.J.: NS-WeM10, 1

Huber, R.C.: NS-WeM6, 1

## — I —

Ilavsky, J.: NS-WeM5, 1

## — J —

Jensen, B.J.: NS-WeM5, 1

Jones, A.: NS-WeM5, 1

## — L —

Lauderbach, L.M.: NS-WeM5, 1

## — M —

May, C.: NS-WeM5, 1

McGuire, G.E.: NS-WeM12, 2

## — N —

Nunn, N.J.: NS-WeM12, 2

## — P —

Podlesak, D.: NS-WeM6, 1

## — R —

Ringstrand, B.: NS-WeM6, **1**

## — S —

Shenderova, O.A.: NS-WeM12, **2**

Simpson, D.: NS-WeM10, **1**

## — T —

Tsai, P.-C.: NS-WeM2, **1**

## — V —

van Buuren, T.: NS-WeM5, 1

## — W —

Watkins, E.: NS-WeM5, 1

Willey, T.M.: NS-WeM5, **1**

Wrachtrup, J.: NS-WeM3, **1**