3D Machine Learning Assisted Correlative Luminescence and Electron Microscopy Revealing Origins of Fluorescent Nanodiamond Brightness Variations

S. L. Y. Chang[1,2] and H. Wen[2]

[1] *Electron Microscope Unit, Mark Wainwright Analytical Centre, University of New South Wales, Sydney, NSW 2052, Australia*

[2] *School of Materials Science and Engineering, University of New South Wales, Sydney, NSW 2052, Australia*

Shery.chang@unsw.edu.au

Fluorescent nanodiamonds (FNDs) are diamond nanoparticles containing light-emitting color centers. Due to the great application prospects in biomedicine, diagnostic and sensing applications, the optical properties of fluorescent nanodiamonds (FND) have been extensively studied. However, FND suffer from low uniformity in their optical properties. For example, it has been reported that the quantum efficiency of FND of nominally same particle size can vary from 10-90% [1]. The complex underlying reasons have been attributed to nanoparticles' atomic-scale structures, including particle shape, size, strain and surface atomic structure and chemistry [2]. In order to realize the usefulness of FND in the above mentioned applications, it is necessary to statistically study the relationship between its structure and optical properties at the individual particle level.

Correlating optical properties with nanoparticles' structures require linking measurements of nearly 3 orders of magnitude difference in length scale. In order to overcome the lack of spatial resolution of optical measurement methods at this stage, the combination of electron microscopy, especially high-resolution TEM, and optical microscopy technology has become an ideal solution.

The biggest challenge in correlating photoluminescence microscopy with TEM to study individual nanoparticle is the accuracy required in overlaying two "maps" that have very different field of view without any bias, distortions that arise from different instrumentation setup. Another challenge is to effectively analyze the structural information from inevitably large data sets required for the TEM images (in order to match the field of view of the optical imaging).

To overcome these challenges, here we have developed a new method based on correlative transmission electron microscopy and photoluminescence (TEMPL). TEMPL allows a direct correlation of the fluorescence brightness and (quasi) three-dimensional size and shape of individual nanoparticles. PL provides optical information with exquisite energy resolution, and TEM provides structural information with exquisite spatial resolution. Unsupervised machine learning (ML), using generalized 3D shape descriptors, is used to analyse correlations between the PL brightness and 3D shape of FND particles. The automation provided by machine learning allows TEMPL to be applied to large sample areas (2-3 orders of magnitude larger than a typical TEM field of view) containing a statistically significant number of particles.

Using the TEMPL method, we have investigated NV containing FND of varying surface treatment and nominal size range. Our results directly reveal that the volume-averaged brightness of thin, flake-like nanodiamond particles is up to seven times greater than that of three-dimensional-shaped, thicker particles. With the assumption that the number of NVs within a particle is proportional to its volume, this implies that individual NVs within thinner particles are brighter. Our theoretical analysis indicates that the comparative brightness of thinner particles, either on a thin supporting substrate or in a low-index medium, is attributable, at least in part, to the constructive interference of partial light waves in these particles. With increasing particle thickness, such an effect becomes damped.

In addition to correlation between PL and TEM, we have expanded our method to other modalities of luminescence including cathodoluminescence as well as SEM and AFM. This allow us to explore substrate effect with thicker substrate that is not applicable in a TEM.

Overall our new methodology provides an deeper insight into the origins of large fluorescent brightness variations in FND. Such insight is critical for improving and controlling the uniformity of FND properties.