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doi:10.1017/S1431927621007601
Microsc. Microanal. 27 (Suppl 1), 2021

Combining in situ micro-photoluminescence and cathodoluminescence to understand defects photophysics in nanodiamonds

Noémie Bonnet[1], François Treussart[2], Huan Chang[3], Mathieu Kociak[4] and Luiz H. G. Tizei[5]

[1]Laboratoire de Physique des Solides/CNRS, Université Paris-Saclay, France, [2]LuMIn/CNRS, Université Paris-Saclay, France, [3]Institute of Atomic and Molecular Sciences/Academia Sinica, Taiwan (Republic of China), [4]CNRS, Orsay, Ile-de-France, United States, [5]Université Paris-Saclay, CNRS, Laboratoire de Physique des Solides, 91405, Orsay, France, France

In this contribution, we will present the results obtained by measuring the luminescence of nitrogen-vacancy (NV) centers in nanodiamonds, excited both by electron beam, cathodoluminescence (CL), and by an out-of-resonance laser, photoluminescence (PL). The measurements have been realized in a scanning transmission electron microscope (STEM), in order to get a nanometer spatial resolution together with PL and CL emission. Superposition of several continuous wave lasers with the electron beam have been achieved to perform optical pumping of the NV centers.

Confocal PL microscopy is a widely used technique that allows for the optical characterization of a wide range of systems, such as single defects or monolayers [1]. However, this technique cannot precisely couple optical measurements to local structural and chemical information [2]. To combine the advantages of the PL and the high-resolution achieved with electron microscopy, we have combined them in a STEM microscope.

Even if CL can be used as the counterpart of out-of-resonance PL [3], some systems show a different behavior when excited with lasers or with electrons. For example, NV centers in diamond exist in several charge-states, including NV^0 (neutral) and NV^- (negatively-charged) [4] that may be excited differently with photons or electrons. CL exhibits typical NV^0 signatures while PL may exhibit both NV^0 and NV^- signatures. NV centers have attracted much interest due to their high stability and brightness, while being quantum emitters with possibility for optical spin readout [5]. Each charge-state has a different optical signature, with a zero-phonon line (ZPL) peak at 575 nm (2.157 eV) for NV^0 and 637 nm (1.947 eV) for NV^-.

To understand the NV excitation mechanism with electrons and why it differs from the optical one, we built a setup combining confocal photoluminescence in a VGHB501 STEM electron microscope, which allows us to conduct PL and CL spectroscopy measurements, together with high resolution imaging (preliminary results are shown in Fig. 1). On top of being a potential universal tool for high-precision characterization of photoactive nanomaterials, the combination of laser and electron beams can help understanding the photophysics of light emitters existing in different charge-state, such as NV centers.

The sample used contains aggregates of sized 100≈nm fluorescent nanodiamonds (FNDs), with high concentration of NV centers. A reference image of a FNDs aggregate laying on a lacey carbon TEM grid is shown in Fig. 1a, and a scheme of the setup is shown in Fig. 1b. The lasers (including a 405 nm UV diode, a 543 nm He-Ne laser, and a 1064 nm solid-state laser) are brought to the sample by a parabolic mirror (NA=0.5) from Attolight Mönch setup [6], and the detection is done in the confocal geometry. The 543 nm laser is used as a reference for PL, while the other two are used as optical pumps to perform charge-transfer on the NV centers. All measurements are done with a 60 keV electron beam energy with the sample kept at 150K.

To superimpose the laser beams onto the electron beam we relied on specific features of CL and PL: in CL, only NV^0 is observed [7], while under 543 nm laser excitation the PL displays both NV^0 and NV^- (Fig. 1c). Since NV^- emission is not detected in CL, it can be used to probe the profile of the excitation, provided the FND aggregate is much smaller (Fig. 1d). Indeed, this aggregate size has to be chosen to match the

displacement reproducibility of our sample moving stage, which is ≈1 µm. The displayed intensity maps in Fig. 1d and e are measured concurrently, with both the electron beam and the laser beam immobile and focused at the same place. The shape of the laser spot is then measured by integrating the NV^- PL signal from 750 to 800 nm, and that of the CL spot, limited by the pixel size, is measured by integrating from 570 to 590 nm. The laser spot is smaller than 3 µm which is what is expected from the diffraction limit of our setup.

In confocal microscopes, several wavelengths are often used to enable characterization of a large variety of samples. In the following, we used two additional lasers to investigate the photophysics of NV centers in the STEM microscope. Under illumination from only a 405 nm cw laser, we observed a similar spectral shape as that seen in CL: the NV^0 peak is present, and NV^- is almost absent (it is completely absent for CL). This could be indicating that the process of charge modification happening in CL is similar to that for produced by high-energy laser excitation.

The infrared (IR) 1064 nm laser was added to the PL excitation (543nm) in order to convert some NV^0 centers to NV^-, as reported previously in PL experiments [8]. We reproduced this PL result successfully at room temperature on a glass cover slit, and obtained a conversion up to 7%, but we failed to observe this effect in the STEM microscope. We think that this could be due to sample overheating because of the small surface contact with the liquid nitrogen stage (from use of lacey carbon TEM grid).

At the time of writing, the system is being adapted to a highly monochromated, aberration-corrected NION Hermes 200, equipped with an Attolight Mönch system. The resolution in imaging with the electron beam should be largely improved. We hope to present related results on other type of emitters at the time of the conference.

Acknowledgements: This project has been funded in part by the National Agency for Research under the program of future investment TEMPOS-CHROMATEM (reference no. ANR-10-EQPX-50) and from the European Union's Horizon 2020 research and innovation programme under grant agreement No 823717 (ESTEEM3). This work has been supported by Region Île-de-France in the framework of the DIM SIRTEQ.

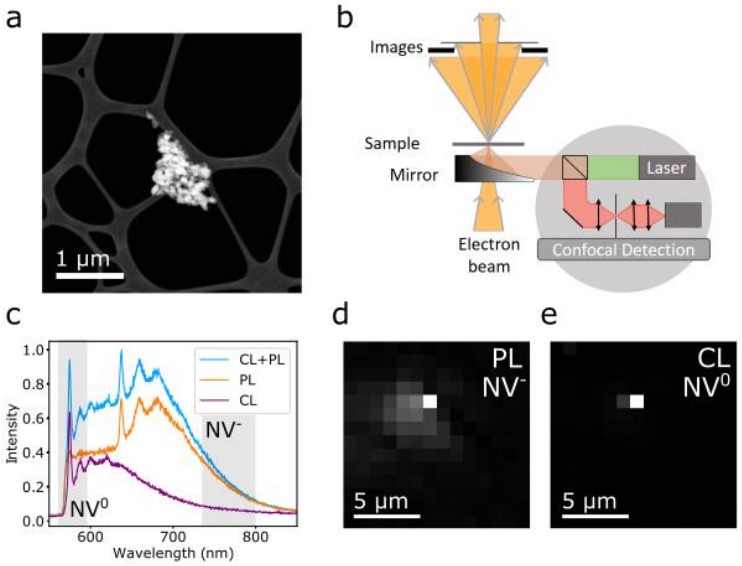

Figure 1. Combined in-situ micro-PL and CL on an aggregate of FNDs: (a) high angle annular dark field image (HAADF) showing an aggregate of size about 1 µm laying of a lacey carbon grid. (b) Scheme of the experiment: the electron beam is transmitted across the sample, allowing for imaging, and the CL light is collected by a parabolic mirror. The lasers are brought to the sample using the same mirror, and the CL and

https://doi.org/10.1017/S1431927621007601 Published online by Cambridge University Press

PL emitted light is separated from laser excitation with a dichroic mirror. The light detected is then dispersed in an optical spectrometer. (c) Typical spectra for CL (blue), PL (orange), CL and PL combined (green) from aggregate (a). The zero-phonon lines (ZPL) of NV0 and NV- are labelled, and the integration range 750-800 nm for NV- intensity and 570-590 for NV0 intensity are highlighted in light grey rectangles, leading respectively to (d) and (e) raster scans. At the 1 µm step size of these scans, we observe that the CL map display mainly one bright pixel, in agreement with the 1 µm-sized aggregates considered and with nanometer scale of the electron beam, while PL raster scan (d) shows a spot extended over about 3 µm, corresponding to the laser beam spot shape.

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