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STEM-CL AND RELATED SPECTROSCOPIES USING A HIGH NUMERICAL APERTURE MIRROR

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1. INTRODUCTION

In 2015, one of us (MK) was invited to give a lecture on STEM-CL. Indeed, the technique was then undergoing a revival, mainly driven by the pioneer group in the field (Prof. Yamamoto's team, now Sannomiya's) and the one at LPS in Orsay. As we noted at the time, this revival also accompanied that of cathodoluminescence in the SEM. At that time, we presented the salient results of a nascent field, and from this course emerged a few years later a journal article on STEM-CL.

The advances obtained in the Orsay STEM group were essentially linked to the possibility of driving, in the reduced and constrained space of the TEM objective lens gap, a high numerical aperture mirror with great precision and reproducibility in the positioning. The common point of the experiments described in this paper and obtained in the teams of the LPS at Orsay and the CEMES in Toulouse is also this mirror, to which innovative technologies are attached. It is worth noting that several authors have financial interests with the Attolight Company, which sells now the mirror as a commercial product.

Figure 1 shows schematically a STEM with a gun (which may or may not be pulsed), possibly a monochromator, a mirror to detect or inject light, and an EELS spectrometer. Depending on its mode of operation, several particles can be detected or injected, in a time-resolved or not, synchronised or not. The main part of this proceeding will concern such correlative, coincident, or synchronized experiments, which is emphasised in Figs. 1 and 2.

7 years back ago, the results concerning the Orsay group presented at EMAS in 2015 were those shown in Fig. 1 and obtained on a VG HB501 microscope, which is now more than 40 years old. Despite its advanced age, results are still being obtained on the VG. But we will mainly present results obtained on the FEMTOTEM microscope from Toulouse (Hitachi microscope on which is mounted a unique pulsed field effect gun) and the CHROMATEM monochromatic microscope (customised version of the NION HERMES200) and summarised on Fig. 2.

As the course was aimed at a SEM-CL community, the content of the course revolved around the competitive advantages of using STEM over SEM. To simplify, we insisted at the time on four points that we will more or less repeat in the presentation of this proceeding:

- The use of high-speed electrons, allowing to obtain a better spatial resolution (Fig. 1, SI STEM-CL). The increase in spatial resolution was evident in the hyperspectral mapping of quantum confined systems [4]. For example, we had shown the possibility of spatially distinguishing two GaN quantum wells separated by a few nanometres in AlN wires. These types of studies, which are still flourishing (see for example [5], will not be discussed in this conference proceedings.
- The possibility of coupling CL to the vast range of STEM techniques. In particular, high-resolution imaging had enabled a quantitative study of the link between emission wavelength and (atomic scale) [4] quantum well size. Perhaps most importantly,

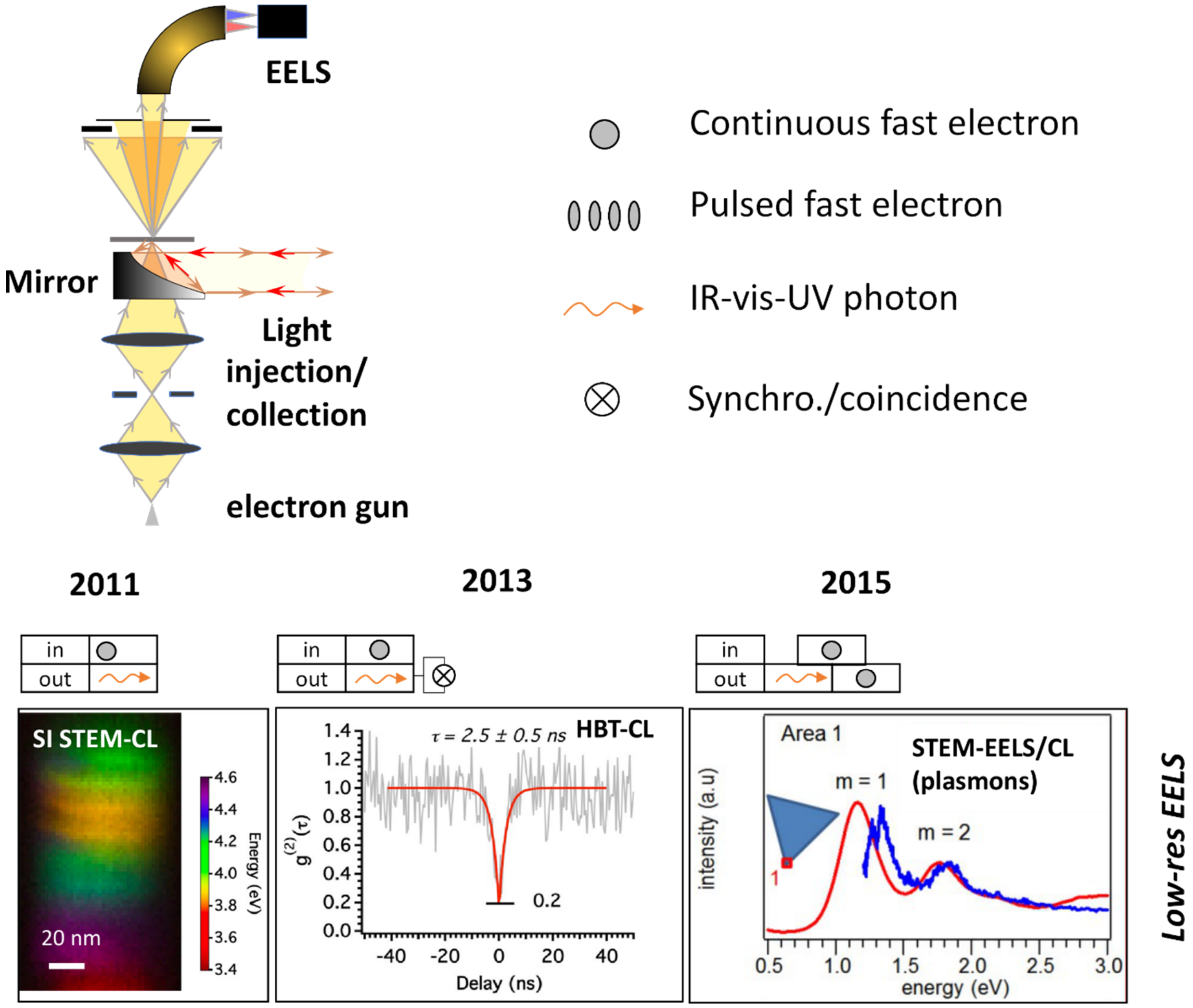

Figure 1. EELS and CL based spectroscopies in (S)TEM, and how they can be combined together. Top, left: Schematics of a (S)TEM fitted with a gun (optionally pulsed), a monochromator (optional), a high numerical aperture mirror for light injection and detection, and an EELS spectrometer. Top, right: Pictogram convention for Fig. 1 (bottom) and Fig. 2. Bottom: Some milestones experiments (from left to right [1-3]), at the time of the lecture on STEM-CL at the 2015 edition of EMAS, obtained on a continuous and non-monochromated VG microscope. SI: spectral-imaging. HBT: Hanbury-Brown and Twiss (intensity) interferometer. "Low-res EELS" stands for the non-monochromated VG microscope.

a comparative study of hyperspectral mapping of plasmons in energy loss spectroscopy (EELS) and CL had demonstrated the intimate links between optical (extinction/scattering) and electronic (EELS/CL) [3] spectroscopies, see Fig. 1. In this extended abstract, we will see how the latest technological developments have made it possible to extend comparative EELS/CL analyses, which were previously limited to plasmons due to the poor spectral resolution of EELS, to optical excitations in semiconductors (figure 2) or nano-photonic systems thanks to the emergence of monochromated machines. For the latter, we will see how

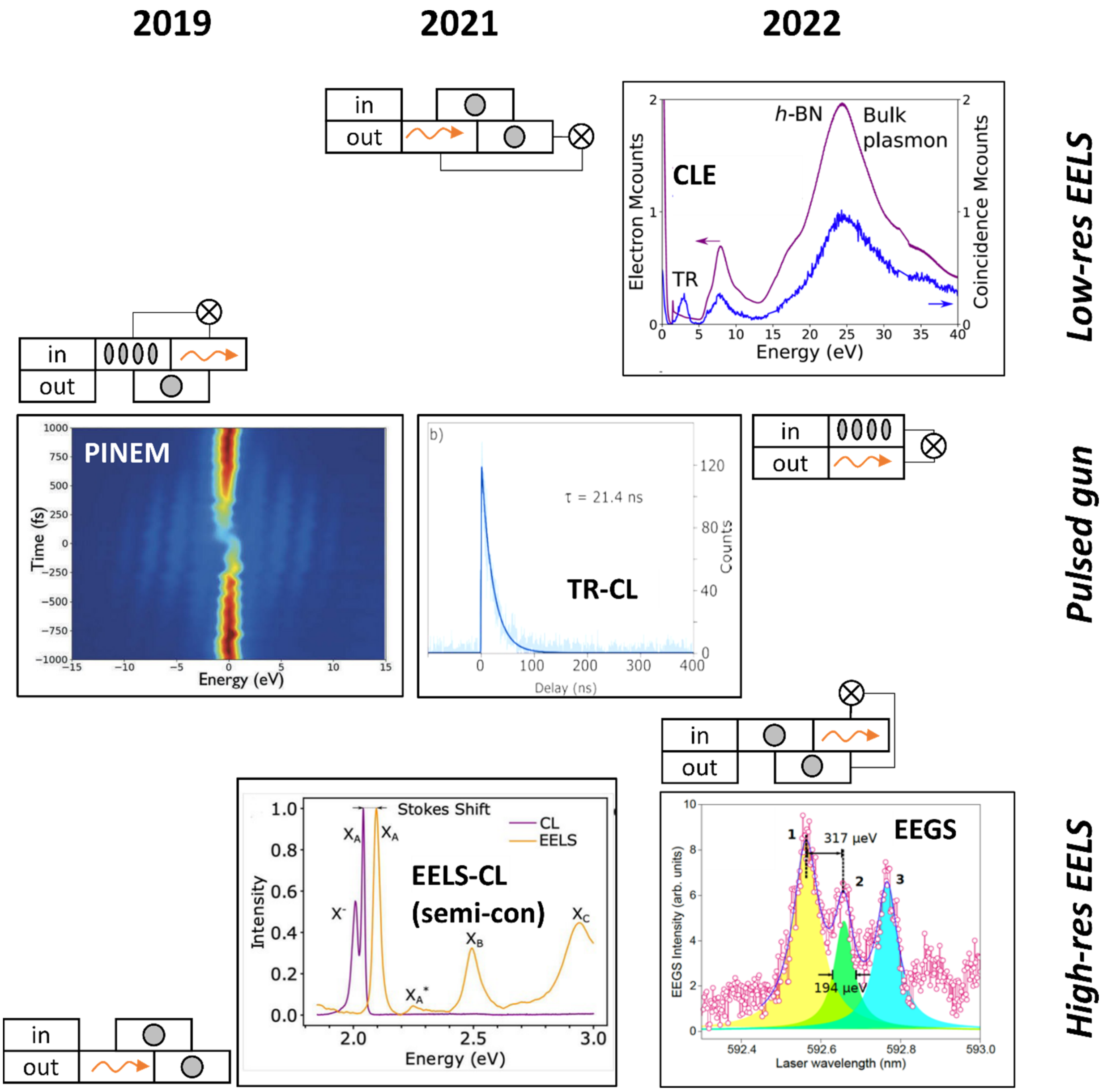

Figure 2 Some milestones experiments (from top to bottom, left to right [8, 10-13]) after the lecture on STEM-CL at the 2015 edition of EMAS. They have been obtained on a continuous and non-monochromated VG microscope, a pulsed gun, non-monochromated Hitachi microscope (FEMTOTEM) and a highly monochromated NION microscope (CHROMATEM). PINEM: photon induced near-field electron microscopy, EEGS: electron energy gain spectroscopy, CLE: cathodoluminescence excitation spectroscopy, TR-CL: time resolved cathodoluminescence. The pictograms convention is given in Fig. 1. ”Pulsed gun” stands for the FEMTOTEM microscope and ”Highres EELS” for the CHROMATEM microscope.

the use of a CL detector to inject light leads to the creation of a new type of spectroscopy with very high spectral resolution (Fig. 2) [6-8], the energy gain spectroscopy (EEGS) directly derived from photon induced near-field electron microscopy (PINEM) spectroscopies [9, 10] (Fig. 2) also possible with our mirror.

- A gentle excitation of the material by high speed electrons, allowing to remain always in a linear excitation regime. This allowed us to demonstrate the similarity between STEM-CL and photoluminescence (PL) in the case of [14] quantum dots. Since then, this feature has been exploited for the study of single-photon emission through auto-correlation experiments using a flagship quantum optics system, the intensity interferometer (HBT) [2] (Fig. 1). This was the first system of its kind for either STEM or SEM. The use of the HBT was unexpectedly successful not only in the STEM, but also especially in the SEM, thanks to the discovery of an effect called ”bunching” [1, 15-17], which allows a measurement of lifetimes at very high spatial resolution, and of which we will say a few words later. The time resolution limitations of HBT motivated the development of time-resolved cathodoluminescence in a TEM by the Toulouse team [12] (Fig. 2). On the other hand, the power of photon-photon coincidence analysis led the Orsay team to develop also an EELS/CL coincidence analysis [11] (Fig. 2), which will be discussed extensively in this proceeding.

2. *CORRELATION BETWEEN EELS AND CL*

In 2015, we showed that EELS and cathodoluminescence were the nanometric equivalents of extinction and diffusion spectroscopy for optics [3]. Moreover, we had shown by comparing CL and PL on the same quantum dot that the two latter gave equivalent luminescence information [14]. It was, therefore, very tempting to extend the analogy valid for plasmons to semiconductors and photonic systems. Unfortunately, this required a much better spectral resolution in EELS than the few hundred meV accessible on an old generation microscope. Indeed, if the FWHM of plasmons in the visible is of the order of a few hundred meV and, therefore, compatible with old generation EELS technologies, the same is not true for excitons and photonic modes. The arrival of high-resolution monochromators [18] changed the situation in the mid-2010s, allowing, in addition to access to the infrared regime, to obtain resolutions below a few meV in the visible.

In Fig. 3a we present the comparison between EELS and CL spectra for a layer of a transition metal dichalcogenide (TMD) two-dimensional semiconductor material (WS_2) [13]. These results are directly comparable to optical absorption and emission results, with the added spatial resolution of course. TMDs have recently become increasingly popular due to their spectacular optical properties. In particular, we can see directly the interest of using two different spectroscopies because they reveal different excitations within the same material. In particular, we have used them to study the formation of trions at the nanoscale [13].

It is also thanks to this generation of monochromators that it is now possible to study photonic structures in EELS [19], and thus to make relevant comparisons between EELS and CL for these systems. We show in Fig. 3b a result obtained on a SiO_2 sphere of micrometres in diameter [8]. In this type of system, it is known that there are modes propagating along the perimeter of the sphere and called WGM (whispering gallery modes). It is easy to see the interest of using both

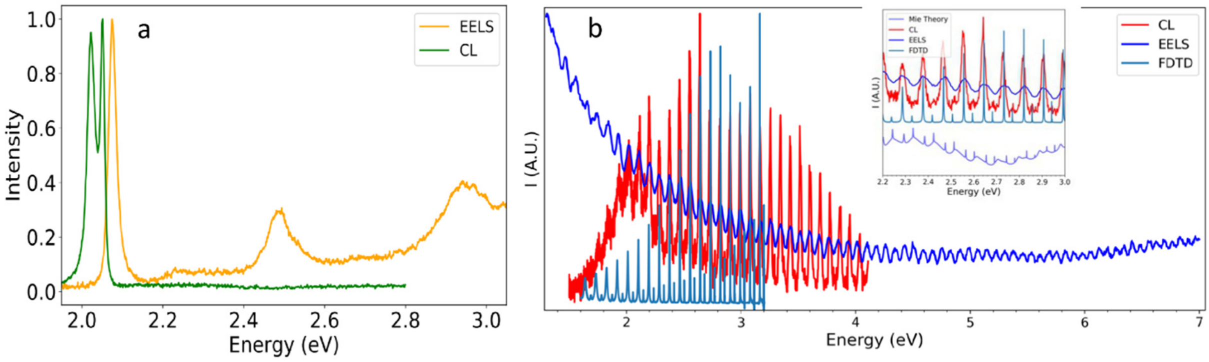

Figure 3. Comparison between EELS and cathodoluminescence (no time-coincidence). a) Typical electron energy-loss spectrum (EELS, orange) and cathodoluminescence (CL, purple) at the same beam position on a WS_2 sample [13]. b) EELS and CL spectra of a µm-sized silica sphere measured by using 200 keV, compared to FDTD simulations. Inset: Enlarged area showing the relatively low EELS resolution.

techniques: EELS allows access to a very wide range of modes whereas CL has only a limited range; however, it is clear that if the signal to noise ratio (SNR) of EELS is much higher than that of CL, only the spectral resolution of the latter allows to resolve the modes (TE and TM).

Despite the undeniable success of monochromation in addition to CL in a STEM, we can see that these techniques are limited in at least two ways. On the one hand, the spectral resolution of EELS and the SNR of CL are too low to expect to study photonic modes with high quality factors. On the other hand, the dynamics of the excitations cannot be studied. The solution to these problems lies in the use of various synchronisation schemes between different signals as explained in Figs. 1 and 2.

3. *LIGHT INJECTION IN THE (S)TEM*

As predicted some 15 years ago, it is theoretically possible to accelerate the electrons by injecting a laser into the sample to pump the sample, creating an excitation that will accelerate the electrons. Such an energy gain is the stimulated counterpart of the energy loss [6]. This effect has been demonstrated using pulsed guns whose emission is synchronised with the illumination of a sample by a femtosecond laser [9]. Until very recently, the high temporal resolution of this type of set-up was not used and it was rather the strong interaction allowed by this type of illumination that was used. Our mirror could thus be used in FEMTOTEM to obtain a PINEM signal (see Fig. 2) [10, 20]. The high numerical aperture requires a detailed simulation [20].

The use of a femtosecond laser, due to the energy-time uncertainty relation, does not allow spectral resolutions better than about 10 meV [21] to be achieved. Although remarkable considering the nominal resolution of the microscopes used, this is far from the necessary resolution (in the order of μeV!). The use of continuous or nanosecond lasers is, therefore, necessary [8]. The first demonstration of energy gain spectroscopy was made by the Ropers team using a continuous laser [7]. The exceptional μeV resolution was, however, only obtained for a dedicated sample. We have recently used our mirror to obtain resolutions of the order of a hundred μeV in the case of an arbitrary Fig. 2 dielectric sphere [8].

Now that we know that we can get rid of the EELS spectral resolution and CL SNR problems with the EEGS, can we study the dynamics of the excitations?

4. LIFETIME MEASUREMENTS IN THE STEM

For this, the most obvious, but probably technology demanding, way is to use a pulsed gun to do cathodoluminescence. This is what was done recently on the FEMTOTEM microscope in Toulouse where it was possible to map the lifetime of point defects in a nano-diamond with a spatial resolution of a few nanometres [12], as shown on Fig. 2 (see also another STEM CL study at low voltage [23]. The lack of current and therefore of photons in STEM compared to SEM makes the experiment particularly complicated, and requires a mirror with a high numerical aperture.

Temporal resolution and dynamic tracking can also be achieved with coincidence methods. We had indeed shown that it was possible to measure the autocorrelation function $g^2(\tau)$ as a function of the delay τ of a cathodoluminescence signal. The measurement of the autocorrelation function is a well-known method in optics to determine the quantum nature, or not, of a radiation. Thus, a value of the autocorrelation function smaller than 1 is the unequivocal signature of a purely quantum effect, in this case the emission of single photons. This effect has been measured by us in the case of single defects in nano-diamonds [2] and hexagonal boron nitride (hBN) [22] (Fig. 4). We also discovered that except for this particular case, the autocorrelation function was in general very large at zero delay [15]. This is one of the rare occasions when the PL and the CL are different. The apparent grouping of photons in CL comes from the fact that in CL it is essentially a volume plasmon which is excited at high energy, and which de-excites very quickly in the form of several pairs of electron holes. The latter can all be de-excited at the same time, producing the synchronised emission of photons; “all at the same time” means “during the typical deexcitation time”. It is, therefore, possible to measure the lifetime of excitations in systems, with ultimately the spatial resolution of STEM-CL [1]. It should be noted that the bunching measurement has been unequivocally successful for the measurement of lifetime [1, 16, 17] and quantum efficiency [16, 17], and especially in SEM. It is indeed a less effective alternative than the TR-SEM-CL, but much less restrictive experimentally because it does not require a pulsed gun or a fast blanker.

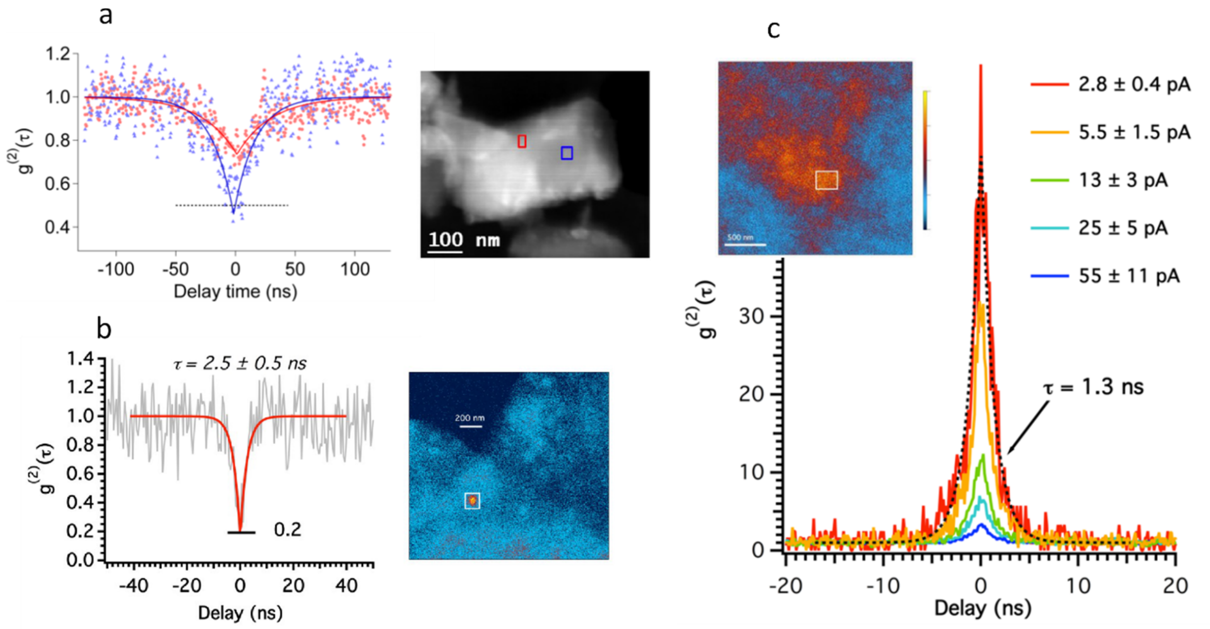

Figure 4. Intensity interferometry. a) $g^2(\tau)$ measurements on a nitrogen-vacancy centre in diamond, taken at two positions indicated on the left high angular dark field image [2]. b) Same for a defect in an h-BN flake, with the CL emission map on the right [22]. c) Same for a collection of the same defects [15]. In a and b) the $g^2(\tau)$ displays anti-bunching, while in c) it displays bunching.

5. CATHODOLUMINESCENCE EXCITATION SPECTROSCOPY

As shown in Figs. 1 and 2, beyond the correlation between signals, the synchronisation and coincidence between them clearly provides unique information. In particular, if the gain measurements (synchronisation between laser and electron) make it possible to obtain a very high spectral resolution, the TR-CL or the bunching measurement (electron-photon or photon-photon correlation) a high temporal resolution, there are still shady areas concerning the dynamics of excitations in materials. Let us take the case of Fig. 3a. We know that the emission of photons (from a trion or exciton) follows an absorption of energy from the incident photon by the material. This absorption is necessarily contained in the EELS spectrum. But we have no way of knowing from which part of the EELS spectrum this energy comes: Is it the X_A exciton? X_B?, etc. In other words, we have no way of knowing how to trace the quantum efficiency of the material. Such a measurement is possible with photoluminescence (see Fig. 5). In this technique (photoluminescence excitation spectroscopy, PLE), a monochromatic laser is used to excite the sample to a well-known energy. After measuring a PLE spectrum, it is then easy to relate the emission process to the absorption process. In the case of CL, the problem is that the electromagnetic field that follows the electron and is responsible for the absorption by the material is essentially white [24] (see Fig. 5). Therefore, it is not possible to establish this link in general. However, in the case where an EELS event can be isolated in time, the situation changes. It is then possible to correlate the detection of an EELS event with that of the emission of a photon, and thus obtain a CLE spectrum [11]. This is shown in the spectrum of Fig. 6a in the case of a hexagonal boron nitride (hBN) flake. In the case of hBN, the EELS spectrum is very different from the cathodoluminescence spectrum. The former is dominated by the absorption band and especially the bulk plasmon, while the latter is essentially dominated by the emission from a defect at 4.1 eV [22]. The CLE spectrum shows us which part of the absorption band creates the most photons. It is indeed the plasmon, as mentioned above. However, by taking the ratio of the CLE and EELS spectra, we can trace the energy-resolved quantum efficiency (Fig. 5c). The intrinsic efficiency of an excitation to create luminescence is then determined, independently of its ability to absorb energy.

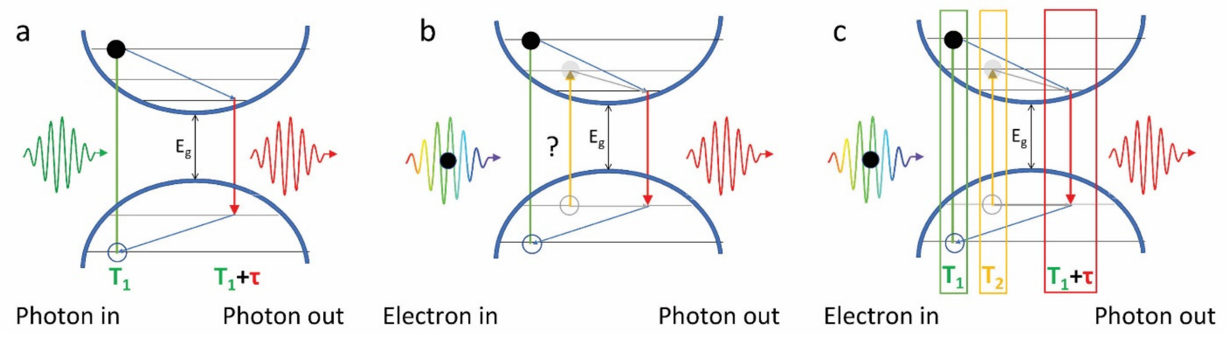

Figure 5. PLE and CLE. a) In PLE, a photon of defined wavelength (green) is absorbed at time T_1. After decay, a photon (red) may be emitted at time $T_1 + \tau$. The path between the excited and de-excited state is easy to follow due to the monochromaticity of the incoming laser beam. b) In a regular EELS/CL experiment, an electron impinges on the sample. A (red) photon is emitted. The electromagnetic field following the electron is broadband, therefore, a set of states can be excited (the green and orange transitions), so it is impossible to follow the path between energy absorption and emission. c) In a CLE experiment, EELS and CL events are time-stamped, linking the photon emission to a specific EELS event at time T ($T = T_1$ in the present example).

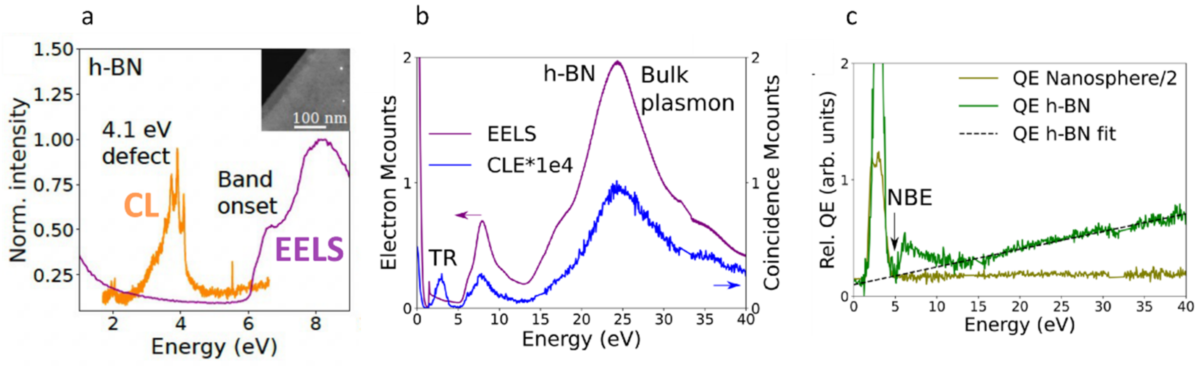

Figure 6. a) CL and EELS spectra of a thin hBN flake. b) EELS and CLE spectra of another h-BN thin flake. c) Relative QE of a plasmonic nanosphere and the thin h-BN flake of b). Near band edge (NBE) losses are more efficient pathways for light emission than energies below the bulk plasmon. Above 15 eV, the relative QE increases linearly. TR: transition radiations. From [11].

6. CONCLUSION AND FUTURE PROSPECTS

We have seen that the use of a high numerical aperture mirror in a STEM is of interest for CL. As soon as the CL signal is correlated with other signals, in particular the EELS, a whole range of new information emerges. The same is true when the mirror is used to inject light. We believe that the various techniques listed are still in their infancy, and that there is much to look forward to. Missing from the toolbox of our STEM-CL system, however, is the ability to polarise the light. This is routinely done in SEM [25], and in some TEM [26] or STEM [27]. In all these cases, the mirrors are either of small numerical aperture and/or of large size, which is not our case. However, we have recently succeeded in installing a cathodoluminescence polarisation system (see Fig. 7), which makes us optimistic about the possibility of generalising the experiments presented above.

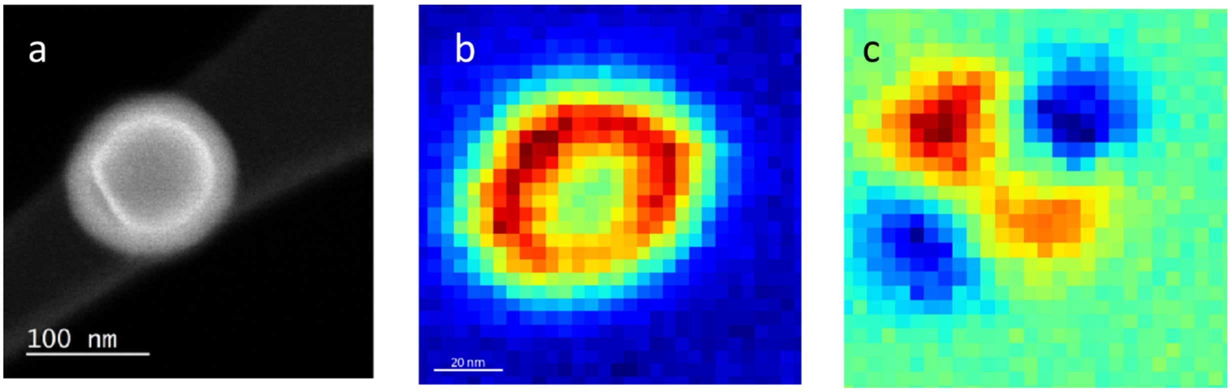

Figure 7. a) High angle annular dark field of a plasmonic sphere covered with a thin shell of silica. b) Non-polarised and c) Lineary polarised CL maps filtered at the wavelength of the dipolar mode. In c) two orthogonal directions have been chosen.

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