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Structure and spectroscopic properties of BN 1D and 2D nanostructures

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Hexagonal boron nitride (h-BN) is a wide band gap semiconductor (6.4eV), which can be synthesized, as its carbon analog graphite, as bulk crystallites, nanotubes and nanosheets. Investigation of their optoelectronic properties is made difficult because of the paucity of high quality samples and suitable investigation tools. These structures meet nevertheless a growing interest for deep UV LED and graphene engineering. A deeper understanding of the interplay between the structural and luminescence properties of different BN structures and how these properties can be further exploited for their characterization are therefore highly needed.
Such studies are now possible thanks to the recent development of dedicated photoluminescence (PL) and cathodoluminescence (CL) experiments running at 4K and adapted to the detection in the far UV range (up to 6eV) [1]. We can also combine various TEM techniques and CL experiments in a FEG-SEM with a spatial resolution of 3nm on the same nano-object. With these tools, we investigated the structure and luminescence of various structures, from high quality crystals [2], exfoliated nanosheets to multi-wall nanotubes [3].

As a result, BN materials present original optical properties, governed by excitonic effects in the 5.5–6eV energy range. Two kinds of excitonic luminescence have been identified and are called S and D lines [4]. As revealed from CL-TEM analyses, D lines are issued from defective areas (Fig 1), so that D/S ratio can be used as a qualification parameter of the defect densitiy [5]. This procedure has been applied to understand the first luminescence studies of few layers individual BN flakes [5].

Concerning nanotubes, CL images reveal that the luminescence in the 5.5–6eV energy range is strongly inhomogenous and oscillating. Thanks to a deep investigation combining different TEM techniques, we have shown that the tubes display a complex twisted faceted structure and that the twist period is correlated with the luminescence oscillations (Fig 2). Furthermore, we could show that excitons, responsible for the spectacular localization of the luminescence, are trapped to specific defects, twisted along with the faceting structure.
Finally, low-loss EELS providing an alternative approach to the nature of electronic excitations [6], we will show how it is an efficient tool to investigate the local structure and optical properties with an energy resolution below 100meV of different BN layers and nanotubes.

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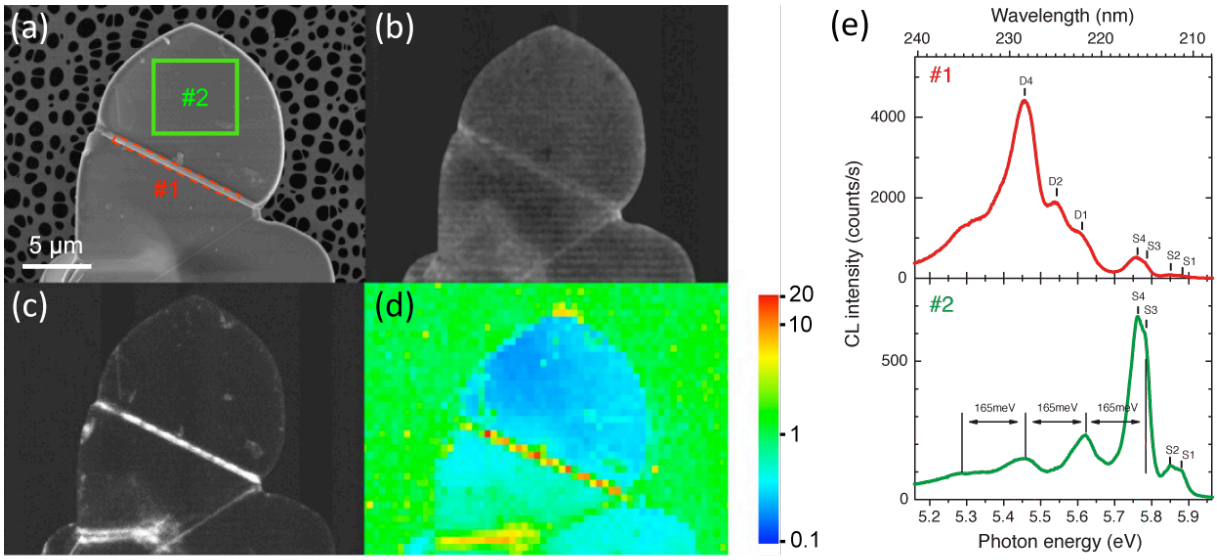

Figure 1: (a) SEM image of a h-BN crystallite; (b), (c) Corresponding CL images recorded (b) on the main S line (S3-S4), and (c) on the main D line (D4). (d) Map of the D/S ratio. (e) CL spectra recorded in the areas #1 (grain boundary) and #2 (middle of the grain), indicated in (a).

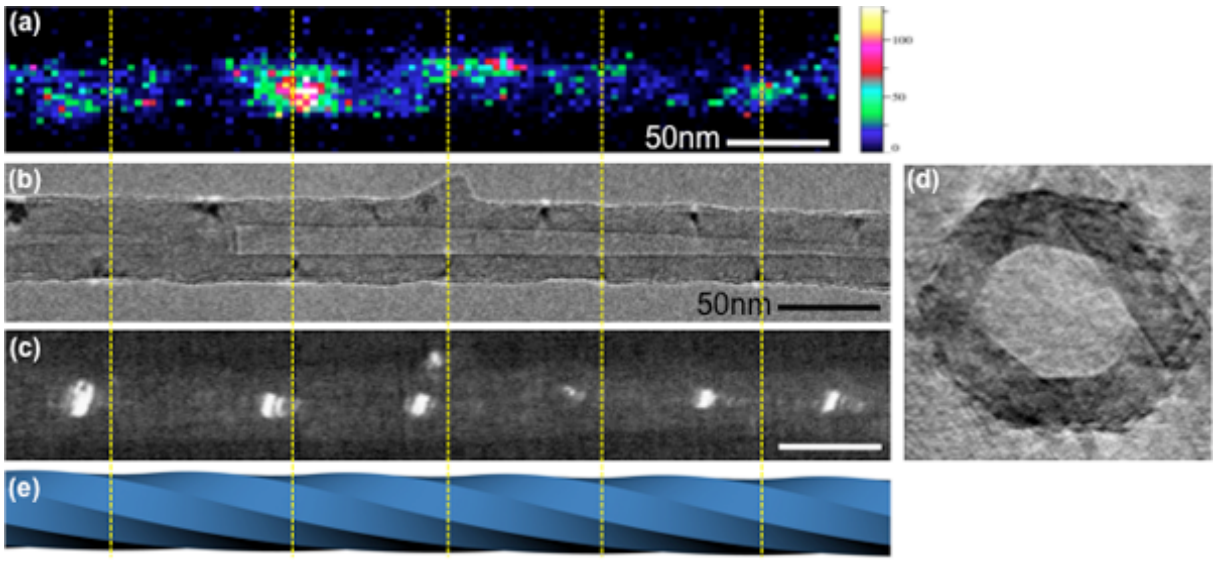

Figure 2: Images of a BN nanotube: (a) 3nm spatially resolved CL image recorded at 5.49 eV (226 nm); (b), (c) Corresponding TEM images in (b) bright-field mode, and (c) dark-field mode on the (100) reflection. (d) Heptagonal tube cross-section obtained by tomography experiment. (e) Structure of the tube as deduced from (b-d) images.