Appendix of CSC 2026 PhD proposal

More detailed document

Better understand h-BN synthesis for its functional optimization

Keywords:

Synthesis processes, crystal growth, Hexagonal Boron Nitride, crystal, TEM, SEM, AFM, 2D-nanomaterial, microstructural, chemical, electroluminescent, characterization

Abstract:

2D-nanomaterials present a remarkable potential to be used for electronic and optoelectronic applications and they have been intensively investigated in the past few years. Graphene is indeed the next potential superstar material for the electronics industry, with a thinner, stronger and much fasterelectron conductor than silicon. However, without any natural energy band-gap, graphene'sconductance cannot be switched off. To overcome this issue, a promising technique is the integration of ultrathin layers of graphene and boron nitride into two-dimensional heterostructures. In this context, availability of well-crystallized h-BN graphene-like nanosheets with high purity and lateral size over 30 μm is a key point in the development of advanced convenient electronic devices. Another innovative solution consists in integrating C sp2 domains into the hexagonal BN (h-BN) sheet, in order to modulate the electronic properties of the material.

For several years now, we became more deeply invested in the preparation of such h-BN based 2D nanomaterials and we recently succeeded in synthesizing self-standing h-BN few- and mono-layers by exfoliation of h-BN single crystals synthesized by combining the Polymer Derived Ceramics route with

a Spark Plasma Sintering (SPS) and further addition of crystallization promoter. Advantage of this dual process is that we may control the two-step synthesis: the chemical preparation

of precursor on the one hand, the crystal growth stage of the resulting powder on the other hand. However, the current BN size remains still insufficient to allow stamping graphene onto BN and some impurities are still detected. In order to increase both the size and purity of product, a new high-pressure crystal growth process is being adapted, which turns out really very efficient to deliver much more larger Boron Nitride Nanosheets (BNNs). However, degrees of freedom of the process are important (purity of reactants, amount of additive agents, yield product, growth temperature-time-ramp-pressure and atmosphere…) and need to be well understood to get well crystallized nanosheets of a few hundred microns. Furthermore, synthesis/processing mechanisms (reactivity between the preceramic precursor and dopants, control and understanding of crystal growth, significance of nucleation sites number and distribution…) have to be better understood and mastered in order to control and improve the h-BN synthesis.

To manage these stages, a fine characterization of each step of the process is proposed during the PhD, in order to highlight critical steps. Besides, to define the key-parameters involved in the synthesis, and better explain their influence on the resulting products (crystallinity, purity, microstructure, properties…), we propose an innovative investigation involving an *in situ* approach. Evolution of the product from its initial polymer-like amorphous state to its final crystallized state will then be followed

by high-temperature XRD, Raman spectroscopy and observed in real-time by environmental electronic microscopies (eSEM, eTEM).

The PhD candidate will be in charge of the synthesis of precursors, sintering of the resulting powder, and characterization of the products. The global investigation (XRD, Raman and IR spectroscopies, cathodoluminescence…) will be completed by a more local complementary approach (SEM, TEM, AFM…). The key-parameters governing the quality of BN-based will be then identified, and modified so that to obtain large BNNs or C-doped BN functional 2D-nanomaterials.

PhD Supervision

The PhD's program can be structured into three different parts: first, synthesis of preliminary solid polymer-like BN by the PDCs route, then, their sintering, followed by their characterization. Therefore, the PhD will be conducted in two laboratories of Lyon city (France):

- Laboratoire des Multimatériaux et Interface (LMI, Université Claude Bernard Lyon1, UMR CNRS 5615),
- Laboratoire MATEriaux Ingénierie et Science (Mateis, INSA de Lyon, UMR CNRS 5510).

Supervision of the Ph-D student will be ensured by one Professor of each laboratory: Bérangère TOURY, from LMI, will be more involved in the chemical synthesis aspects, while Philippe STEYER, from the MATEIS lab, will be more concerned by the deep characterization of the resulting materials.
Taking into account the high multi-disciplinary character of the study, supervision will also be shared with two other colleagues of both laboratories, specialists in C-based nanomaterials (Pr. Catherine JOURNET-GAUTIER) and in ceramics-shaping process (Dr. Vincent GARNIER).

Some of their relevant recent papers appear below:

1. S. Yuan, S. Linas, C. Journet, P. Steyer, V. Garnier, G. Bonnefont, A. Brioude, B. Toury**, Pure & crystallized 2D BN sheets synthesized via a novel process coupling both PDCs and SPS methods,** *Scientific reports*, **6** (*2016) 20388.*
2. S. Yuan, C. Journet, S. Linas, V. Garnier, P. Steyer, S. Benayoun, A. Brioude, B. Toury, **How to Increase the h-BN Crystallinity of Microfilms and Self-Standing Nanosheets: A Review of the Different Strategies Using the PDCs Route,** *Crystals, **6** (2016) 55.*
3. Y. Li, V. Garnier, C. Journet, J. Barjon, A. Loiseau, I. Stenger, A. Plaud, B. Toury, P. Steyer, **Advanced synthesis of highly crystallized hexagonal boron nitride by coupling polymer-derived ceramics and spark plasma sintering processes—influence of the crystallization promoter and sintering temperature**, *Nanotechnology*, **30** (2018) 035604
4. Y. Li, V. Garnier, , P. Steyer, C. Journet, B. Toury, **Millimeter-Scale Hexagonal Boron Nitride Single Crystals for Nanosheet Generation**, *ACS Applied Nano Materials*, **3** (2020)
5. A Pierret, D Mele, H Graef, J Palomo, T Taniguchi, K Watanabe, Y Li, B Toury, C Journet, P Steyer, V Garnier, A Loiseau, J-M Berroir, E Bocquillon, G Fève, C Voisin, E Baudin, M Rosticher and B Plaçais, **Dielectric permittivity, conductivity and breakdown field of hexagonal boron nitride**, *Materials Research Express*, **9** (2022) 065901
6. S. Roux, C. Arnold, E. Carré, E. Janzen, J. H Edgar, C. Maestre, B. Toury, C. Journet, V. Garnier, P. Steyer, T. Taniguchi, K. Watanabe, A. Loiseau, J. Barjon, **Surface recombination and out-of-plane diffusivity of free excitons in hexagonal boron nitride**, *Physical Review B*, **109** (2024) 155305
7. C. Maestre, P. Steyer, B. Toury, C. Journet, V. Garnier, **Hexagonal Boron Nitride Crystal Growth in the Li3BN2-BN System**, *Chemistry of Materials*, **36** (2024) 9848
8. L. Abou-Hamdan, … C. Maestre, C. Journet, B. Toury, V. Garnier, P. Steyer, … E. Baudin, **Electroluminescence and energy transfer mediated by hyperbolic polaritons**, *Nature*, **639** (2025) 909

Whatever your questioning, please, do not hesitate to contact us for further information:

Philippe.steyer@insa-lyon.fr