

Appendix of CSC 2018 PhD proposal

More detailed document

Breakthrough in h-BN graphene-like nanosheets synthesis and future applications

Keywords:

Polymer Derived Ceramics route, sintering processes, hexagonal boron nitride, graphene, environmental SEM and TEM, 2D-nanomaterial, chemical synthesis, *in situ* real-time investigation, microstructural and chemical 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 faster electron conductor than silicon. However, without any natural energy band-gap, graphene's conductance 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 sp^2 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 (see ref. 1-3). Advantage of this dual process is that we may control the two-step synthesis: the chemical preparation of precursor on the one hand, the sintering 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 sintering-based 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, sintering temperature, pressure and atmosphere...) and need to be optimized to get 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 MATériaux Ingénierie et Science (Mateis, INSA de Lyon, UMR CNRS 5510).

Supervision of the Ph-D student will be ensured by one doctor 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 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*, Volume 6, 2016, Page 20388.
2. S. Yuan, B. Toury, C. Journet, A. Brioude, **Synthesis of hexagonal boron nitride graphene-like few layers**, *Nanoscale*, 2014, 6, 7838-7841
3. 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, Page 55.
4. M. Faustini, A. Cattoni, J. Peron, C. Boissière, P. Ebrard, A. Malchère, P. Steyer, D. Grosso, **Dynamic Shaping of Femtoliter Dew Droplets**, *ACS Nano*, 12, 2018, Pages 3243-3252
5. S. Yuan, S. Benayoun, A. Brioude, O. Dezellus, B. Beaugiraud, B. Toury, **New potential for preparation of performing h-BN coatings via polymer pyrolysis in RTA furnace**, *Journal of the European Ceramic Society*, Volume 33, Issue 2, 2013, Pages 393-402
6. H. Termoss, B. Toury, A. Brioude, J. Dazord, J. Le Brusq, P. Miele, **High purity boron nitride thin films prepared by the PDCs route**, *Surface and Coatings Technology*, Volume 201, Issue 18, 2007, Pages 7822-7828
7. A. Etienne, C. Der Loughian, M. Apreutesei, C. Langlois, S. Cardinal, J-M. Pelletier, J-F. Pierson, P. Steyer, **Innovative Zr-Cu-Ag thin film metallic glass deposited by magnetron PVD sputtering for antibacterial applications**, *Journal of Alloys and Compounds*, 707, 2017, 155-161.
8. L. Lallemand, N. Roussel, G. Fantozzi, V. Garnier, G. Bonnefont, T. Douillard, B. Durand, S. Guillemet-Fritsch, J.-Y. Chane-Ching, D. Garcia-Gutierrez, J. Aguilar-Garib, **Effect of amount of doping agent on sintering, microstructure and optical properties of Zr- and La-doped alumina sintered by SPS**, *Journal of the European Ceramic Society*, Volume 34, Issue 5, May 2014, Pages 1279-1288

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

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