SYNTHESIS AND CHARACTERISATION OF BOROPHENE
SYNTHESE ET CARACTERISATION DE BOROPHENE

PhD advisor — Pr. Catherine Journet, catherine.journet@univ-lyon1.fr, 04 72 43 35 64
PhD co-advisors — Dr. Colin Bousige, colin.bousige@univ-lyon1.fr, 04 72 43 36 22
Dr. Catherine Marichy, catherine.marichy@univ-lyon1.fr, 04 72 43 17 01

Laboratoire des Multimatériaux et Interfaces (LMI), UMR 5615, Université Claude Bernard Lyon 1-CNRS

Key words: Atomic Layer Deposition, 2D materials, Borophene, Synthesis/Characterization, Boron

Since the first isolation of graphene in 2004 [1], the scientific community has moved towards new 2D materials with (more) interesting properties. As a matter of fact, despite its numerous qualities that have made it a champion of 2D materials, graphene is still a semi-metal, and until now, no stable 2D material with metallic behavior had been identified. Recently however, it was theoretically demonstrated that a mono-atomic 2D layer of boron, borophene, would present such a metallic behavior with a relatively high electron mobility [2,3]. Moreover, borophene would possess a 100% optical transmittance in the visible range – which would make borophene more transparent than graphene [3]. Interestingly, the chemical boron–boron bond is almost as strong as the carbon-carbon one, and borophene would thus possess mechanical properties close to the ones of graphene [4]. Borophene should also be super-stretchable and super-flexible, it should present stress-induced allotropic transitions [5–7] and even a superconducting behavior [8,9]. Combining all these properties (Figure 1), borophene could be an excellent candidate for use as an anode [10,11] or electrical contact [12].

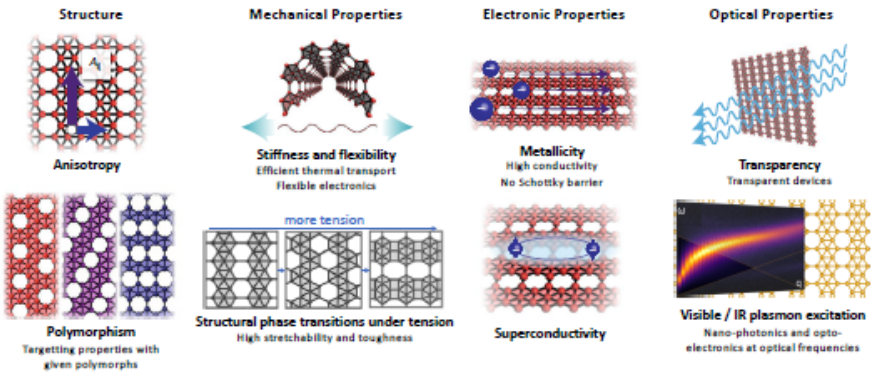

Figure 1: *Summary of the various properties of borophene*

The first attempts at synthesizing boron-based planar structure were focused on the production of small molecular clusters, such as B_{30}^-, B_{35} and B_{36} [13–16], that were thought of as building blocks for larger borophene structures. In 2015 [17] and then again in 2016 [18], the first borophene flakes were grown by epitaxy on silver(111) surfaces in ultra-high vacuum conditions. Atomic-scale

characterization showed that these borophene islands possess metallic characteristics that are compatible with the theoretical predictions of a highly anisotropic 2D metal [2,17]. These results, combined with the intrinsic potential properties of borophene, have led to considerable interest for this material, and especially for applications in energy storage: from 5 publications about this material in the span 2014-2015, it went to 40 in 2016 to reach 60+ in 2017 – mainly from China and the USA. Until now, only theoretical studies were performed in Europe, and there is still a lot to do for optimizing and mastering the synthesis of this 2D material. Moreover, as the current synthesis method does not allow for covering large surfaces and requires ultra-high vacuum, the scientific community is still limited in its ability to experimentally study borophene and to develop its potential applications. There is therefore a very strong need, expressed by the international community of both experimentalists and theoreticians, for easily manipulated borophene samples of large surface and good quality.

Following a previous PhD work with the same supervisors where it was shown that the deposition of thin films of boron rich B_xC with tunable B:C ratio was possible via Plasma Enhanced Atomic Layer Deposition (PEALD), the LMI recruits a PhD candidate to start studying the synthesis of borophene via a new "soft" chemical method (PEALD). This method should allow covering large surfaces of different substrates within a precise environment and with an atomic-scale thickness control. Optimizing the synthesis parameters will however necessitate an in-depth characterization of the obtained structures, using different microscopy and spectroscopy techniques useful for the characterization of ultra-thin layers (STM, AFM, SEM, TEM, XPS, XRD, Raman...). The candidate will benefit of the short feedback loop possible at the LMI and University Lyon 1, thanks to the local expertise in ALD and boron chemistry (C. Marichy), CVD and electron microscopies (C. Journet), as well as numerical simulations (C. Bousige [19]). A number of national and international collaborations will be established to perform the experimental and theoretic studies that we will not be able to achieve locally. As the LMI is implicated in the Nanotube-Graphene GDRi (through C. Journet), we will be in direct contact with a large international community that will be awaiting our samples. Locally, the links already existing with the neighbor Institut Lumière Matière will facilitate some studies, e.g. for electronic and thermal transport or for the mechanical properties.

References:

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Electric Field Effect in Atomically Thin Carbon Films*, Science **306**, 666 (2004).

[2] H. Tang and S. Ismail-Beigi, *Novel Precursors for Boron Nanotubes: The Competition of Two-Center and Three-Center Bonding in Boron Sheets*, Phys. Rev. Lett. **99**, 115501 (2007).

[3] A. Lherbier, A. R. Botello-Méndez, and J.-C. Charlier, *Electronic and Optical Properties of Pristine and Oxidized Borophene*, 2D Mater. **3**, 045006 (2016).

[4] M. Q. Le, B. Mortazavi, and T. Rabczuk, *Mechanical Properties of Borophene Films: A Reactive Molecular Dynamics Investigation*, Nanotechnology **27**, 445709 (2016).

[5] B. Mortazavi, O. Rahaman, A. Dianat, and T. Rabczuk, *Mechanical Responses of Borophene Sheets: A First-Principles Study*, Phys. Chem. Chem. Phys. **18**, 27405 (2016).

[6] Z. Pang, X. Qian, Y. Wei, and R. Yang, *Super-Stretchable Borophene*, EPL Europhys. Lett. **116**, 36001 (2016).

[7] Zhang Zhuhua, Yang Yang, Penev Evgeni S., and Yakobson Boris I., *Elasticity, Flexibility, and Ideal Strength of Borophenes*, Adv. Funct. Mater. **27**, 1605059 (2017).

[8] E. S. Penev, A. Kutana, and B. I. Yakobson, *Can Two-Dimensional Boron Superconduct?*, Nano Lett. **16**, 2522 (2016).

[9] M. Gao, Q.-Z. Li, X.-W. Yan, and J. Wang, *Prediction of Phonon-Mediated Superconductivity in Borophene*, Phys. Rev. B **95**, (2017).

[10] Y. Zhang, Z.-F. Wu, P.-F. Gao, S.-L. Zhang, and Y.-H. Wen, *Could Borophene Be Used as a Promising Anode Material for High-Performance Lithium Ion Battery?*, ACS Appl. Mater. Interfaces **8**, 22175 (2016).

[11] H. R. Jiang, Z. Lu, M. C. Wu, F. Ciucci, and T. S. Zhao, *Borophene: A Promising Anode Material Offering High Specific Capacity and High Rate Capability for Lithium-Ion Batteries*, Nano Energy **23**, 97 (2016).

[12] L. Z. Liu, S. J. Xiong, and X. L. Wu, *Monolayer Borophene Electrode for Effective Elimination of Both the Schottky Barrier and Strong Electric Field Effect*, Appl. Phys. Lett. **109**, 061601 (2016).

[13] W.-L. Li, Y.-F. Zhao, H.-S. Hu, J. Li, and L.-S. Wang, *[B30]−: A Quasiplanar Chiral Boron Cluster*, Angew. Chem. Int. Ed. **53**, 5540 (2014).

[14] W.-L. Li, Q. Chen, W.-J. Tian, H. Bai, Y.-F. Zhao, H.-S. Hu, J. Li, H.-J. Zhai, S.-D. Li, and L.-S. Wang, *The B_{35} Cluster with a Double-Hexagonal Vacancy: A New and More Flexible Structural Motif for Borophene*, J. Am. Chem. Soc. **136**, 12257 (2014).

[15] C.-S. Liu, X. Wang, X.-J. Ye, X. Yan, and Z. Zeng, *Curvature and Ionization-Induced Reversible Hydrogen Storage in Metalized Hexagonal B36*, J. Chem. Phys. **141**, 194306 (2014).

[16] Z. A. Piazza, H.-S. Hu, W.-L. Li, Y.-F. Zhao, J. Li, and L.-S. Wang, *Planar Hexagonal B36 as a Potential Basis for Extended Single-Atom Layer Boron Sheets*, Nat. Commun. **5**, (2014).

[17] A. J. Mannix et al., *Synthesis of Borophenes: Anisotropic, Two-Dimensional Boron Polymorphs*, Science **350**, 1513 (2015).

[18] B. Feng, J. Zhang, Q. Zhong, W. Li, S. Li, H. Li, P. Cheng, S. Meng, L. Chen, and K. Wu, *Experimental Realization of Two-Dimensional Boron Sheets*, Nat. Chem. **8**, 564 (2016).

[19] P. Mignon, A.-R. Allouche, N. R. Innis, and C. Bousige, *Neural Network Approach for a Rapid Prediction of Metal-Supported Borophene Properties*, J. Am. Chem. Soc. **145**, 27857 (2023).