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## COMMUNICATION

## Synthesis of Hexagonal Boron Nitride Graphene-Like Few Layers

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**Self-standing highly crystallized hexagonal boron nitride (h-BN) mono-, bi- and few-layers have been obtained for the first time via the Polymer Derived Ceramics (PDCs) route by adding lithium nitride (Li<sub>3</sub>N) micro powders to a liquid state polyborazylene (PBN). Incorporation of Li<sub>3</sub>N as crystallization promoter allows the onset of crystallization of h-BN at a lower temperature (1200°C) than under classical conditions (1800°C). The hexagonal structure was confirmed by both electron and X-ray diffraction.**

Since the award of the Nobel Prize to Geim and Novoselov in 2010, research on graphene has continued to intensify. Interest in graphene is driven by its remarkable transport properties which make it a good candidate to replace silicon in certain areas, especially when large mobility is required for both electrons and holes. In this way, graphene appears to offer large promises for applications in flexible electronics. However, marketable applications are still far away because, in practice, graphene layers need to be deposited on dielectric substrates, usually SiO<sub>2</sub>, as it has been proved experimentally and theoretically that the suspended graphene sheets with few layers (typically inferior to 10 layers) are thermodynamically unstable.<sup>1</sup> SiO<sub>2</sub> surface imperfections (roughness, charged traps...) significantly affect the carrier mobility. The promising future development of practical graphene devices seems therefore strongly linked to the choice of the substrate. One of the most suitable substrates appears to be hexagonal boron nitride (h-BN, also called “white graphite”), which is isostructural/isolectronic with graphene with a lattice matching the one of graphene. It can also lead to the realization of graphene/BN heterostructures which further expand the field of possible applications.<sup>2,3,4</sup> Recent works<sup>5,6</sup> even suggest the possibility of designing stacked heterostructures in which h-BN and exfoliated graphene flakes are repeatedly stacked on top of each other forming vertically-oriented graphene-based transistors. For such applications, it is highly desirable to precisely control the thickness of h-BN layer-by-layer. Literature reports many different processes for producing h-BN thin films: sputtering<sup>7</sup>,

Pulsed Laser Deposition (PLD)<sup>8,9</sup>, Atomic Laser Deposition (ALD)<sup>10</sup>, Chemical Vapor Deposition (CVD)<sup>11-16</sup> and Polymer Derived Ceramics (PDCs)<sup>17-23</sup>. This last way uses a polymeric precursor, possibly additivated, which has to be converted into ceramic. It remains the most versatile process and allows preparing samples with or without substrate from a polymeric precursor. Among all available precursors, recent works have shown that the use of polyborazylene (PBN) is the best alternative,<sup>24-28</sup> probably due to its easy and reproducible synthesis, combined with its relatively high ceramic yield and high purity. Moreover, the ratio B/N within the polymer is ideal to get further stoichiometric h-BN and there is no contaminant except hydrogen atoms easily removable during the ceramisation step. Finally, the hexagonal arrangement of h-BN is already present within the structure with the borazinic rings. However, this technique usually produces layers with a relatively low h-BN crystallization rate. Consequently, it is important to increase the final crystallization rate of h-BN and we have recently shown that the incorporation of a crystallization promoter into the polymeric precursor before the annealing step allows achieving higher crystallinity at low annealing temperature. In previous work, Li<sub>3</sub>N has been reported to have a catalytic effect for the conversion of h-BN to c-BN at relatively low temperature (600 – 1400°C) and pressure (0.65 - 6.5 GPa).<sup>29-32</sup> Very recently, we demonstrated that lithium nitride also plays a key role in the BN crystallization from PBN allowing crystallinity enhancement at very low temperatures (from 1000°C).<sup>33</sup> This is why we decided to use lithium nitride (Li<sub>3</sub>N) as crystallization promoter. In this paper, we demonstrate for the first time that free-standing highly crystallized hexagonal boron nitride mono-, bi- or few-layers can be obtained by the PDCs route at relatively low temperature compared to previous works. Moreover, we point out that this innovative process does not need any heavy exfoliation process.

### EXPERIMENTAL PROCEDURE

First, pure borazine was obtained from a reaction between ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 99% purity, Aldrich,) and sodium

borohydride ( $\text{NaBH}_4$ , 98% purity, Aldrich) in tetraglyme heated up to  $120^\circ\text{C}$  following a procedure described elsewhere.<sup>34</sup> Borazine purification was performed twice by distillation. The liquid-state polymeric precursor was then obtained by condensation of borazine at  $50^\circ\text{C}$  inside a pressure-sealed system in an argon atmosphere for 5 days, generating a colorless polyborazylene (PBN). PBN was kept below  $4^\circ\text{C}$  to exclude further polymer reticulation. Lithium nitride ( $\text{Li}_3\text{N}$ , Aldrich) micro powder in 5 wt% was added to PBN and the mixture was kept 10 minutes under stirring in a schlenk tube under argon. Suspension of  $\text{Li}_3\text{N}$ -PBN was slowly heated in a schlenk tube under argon from room temperature to  $200^\circ\text{C}$  and held at  $200^\circ\text{C}$  for 1h leading to a solid-state polymer and avoiding oligomer evaporation. The stabilized polymer was then placed in an alumina crucible and was heated at higher temperature ( $1400^\circ\text{C}$ ) ( $1^\circ\text{C}/\text{min}$ ), still under  $\text{N}_2$ , and kept at the final temperature for 1h. White powder is obtained with a 82% mass yield. The raw powder was first analyzed using Raman scattering (the main Raman band of the silica peak is located at  $520.1\text{ cm}^{-1}$ ) and X-Ray diffraction. Then the sample was simply dispersed in ethanol by ultrasonication (1 min at 25 W, Hielscher UP400S) and suspended on a 300 mesh holey carbon copper grid in order to perform HRTEM observation.

## RESULTS AND DISCUSSION

After growth, Raman scattering measurements were collected with an XY Dilor triple spectrometer ( $534\text{ nm}$ ,  $8\text{ mW}$ ) followed by a nitrogen-cooled CCD (Charge Coupled Device) multichannel detector. Raman spectrum presented on figure 1 is typical of h-BN, with a unique signal at  $1367\text{ cm}^{-1}$ , characteristic of the  $\text{E}_{2g}$  mode peak of BN. Since Nemanich *et al.*<sup>35</sup> report relationships between peak broadening (FWHM) and peak shifting of the  $\text{E}_{2g}$  mode signal compared to theoretical value expected for high crystalline h-BN, and the average crystalline size along the a-axis. Considering the slight shift ( $2\text{ cm}^{-1}$ ) and the weak FWHM ( $40\text{ cm}^{-1}$ ) values of this peak, one can assume the good ceramic crystallinity of the h-BN sample.

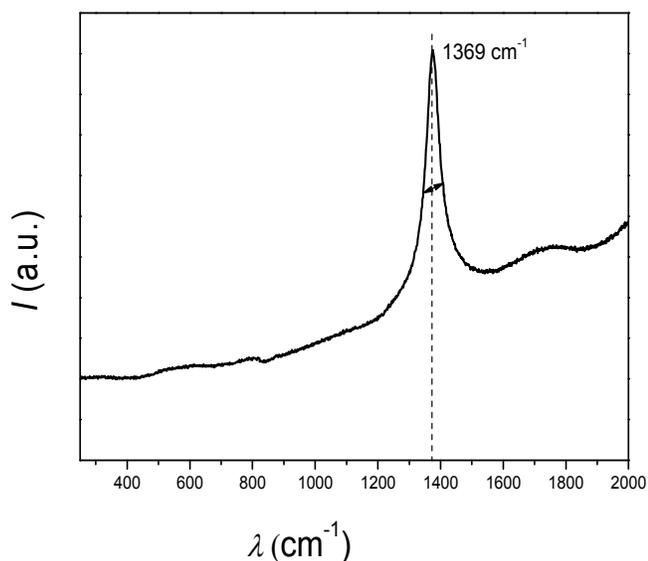


Figure 1: Raman scattering spectrum recorded on our sample, showing a unique signal characteristic of the  $\text{E}_{2g}$  mode peak of BN.

X-ray diffraction (XRD) analysis (Phillips PW 1830/40) with a  $\text{CuK}$  radiation source was performed at room temperature. Recorded diffractogram is presented on Figure 2 and compared to a

commercial h-BN sample as reference.<sup>36</sup> The pattern of this latter displays all diffraction peaks expected for high crystallized h-BN, at  $2\theta = 26.9^\circ, 41.8^\circ, 44^\circ, 50.3^\circ, 55.2^\circ, 75.9^\circ$  and  $82.1^\circ$  corresponding to crystallographic (002), (100), (101), (102), (004), (110) and (112) respectively according to the JCPDS file 034-0421. Regarding to our sample, all these peaks can be found except (102). Normalization of the different peaks by the most intense one *i.e.* (002) allows to achieve their relative intensities (table 1).

	(100)	(101)	(102)	(004)	(110)	(112)
Th. intensity	15	6	15	6	5	5
Cal. intensity	3.7	2.5	0	5	2.8	2

Table 1: Relative intensities of the different peaks normalized by the most intense one

Actually, the ratio of intensities of each peak can be correlated with the area of the coherent diffraction fields. Firstly, it has to be noticed that the theoretical and commercial patterns are identical demonstrating that the commercial sample is well polycrystalline. Secondly, for our sample, only (002) and (004) peaks reach the theoretical values while all the other intensities are lower. This behavior is typical of a crystallite growth along a preferential (002) direction. These results predict the preparation of materials with 2D dimension which is confirmed by HRTEM observation hereafter.

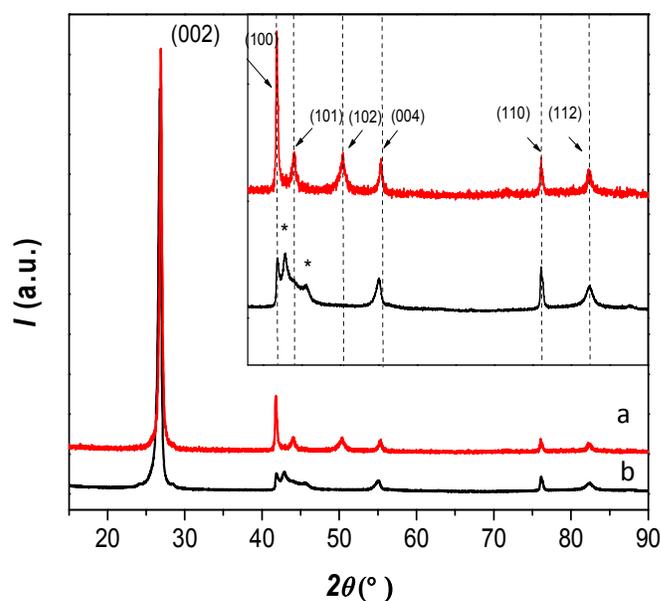


Figure 2: XRD pattern recorded on (a) commercial h-BN (red line) and (b) our sample (black curve) demonstrating high crystallized h-BN. Inset shows amplified signals ( $\times 3$ ).

Meanwhile, two supplementary peaks can also be found at  $2\theta = 42.6^\circ$  and  $45.6^\circ$ . They can be attributed to rhombohedra BN (r-BN) and are marked with stars (JCPDS file 045-1171). It is well known that the structure of r-BN is similar to that of h-BN with a stacking of alternative atomic layers ABC-ABC instead of AB-AB for h-BN.<sup>37-39</sup> The interlayer lattice  $d_{002}$  value measured for this sample is close to the theoretical one ( $3.33\text{ \AA}$  vs  $3.31\text{ \AA}$ ) meaning a good crystallization rate. Moreover,  $\text{Li}_3\text{N}$  or lithium-derived products are not visible. This is not surprising, as we demonstrated in a very recent paper<sup>33</sup> the reaction occurring between PBN and  $\text{Li}_3\text{N}$  leads to  $\text{Li}_3\text{BN}_2$  which displays a melting temperature less than  $1000^\circ\text{C}$  explaining its removal at  $1400^\circ\text{C}$ . In order to confirm the

microstructure of the sample, structural characterization was performed using High Resolution Transmission Electron Microscopy (HR-TEM) with a JEOL 2100F microscope operating at 200 kV (from Centre Technologique des Microstructures, University Claude Bernard Lyon 1). Figure 3a is a representative micrograph obtained on the sample. Many large crystalline areas, with typical crystallite size more than hundreds of nanometers, are visible. The diffraction pattern (inset) shows bright and fine discontinuous rings corresponding to the crystallographic planes of the  $sp^2$  BN phase, which is in good agreement with XRD results. It can be seen that the central area of wide sheets is homogeneous and featureless. Even if several dark lines are experimentally observed on the edges, one has to be very careful because scrolls and multiple folds can give rise to

any number of dark lines even for monolayer h-BN. (see supporting information) The electron diffraction patterns taken on different areas of the flake show that it is a single crystal without domain meaning the sheet folds over itself. In figure 3b, HRTEM on a fine zone of this sheet shows the hexagonal lattice characteristic from the in-plane arrangement and we find that two layers are stacked in a turbostratic position as demonstrated by the Moiré pattern in the atomic scale image showing a lack of AB stacking registry between the two layers (figure 3b). In the inset, the FFT pattern from this Moiré shows two sets of hexagonal spots rotated with an angle of  $12^\circ$ , indicating a two layer region with one layer relatively rotated from  $12^\circ$  with respect to the other one. Using the FFT spot, we can reconstruct the hexagonal atomic network, as shown in figure 3c.

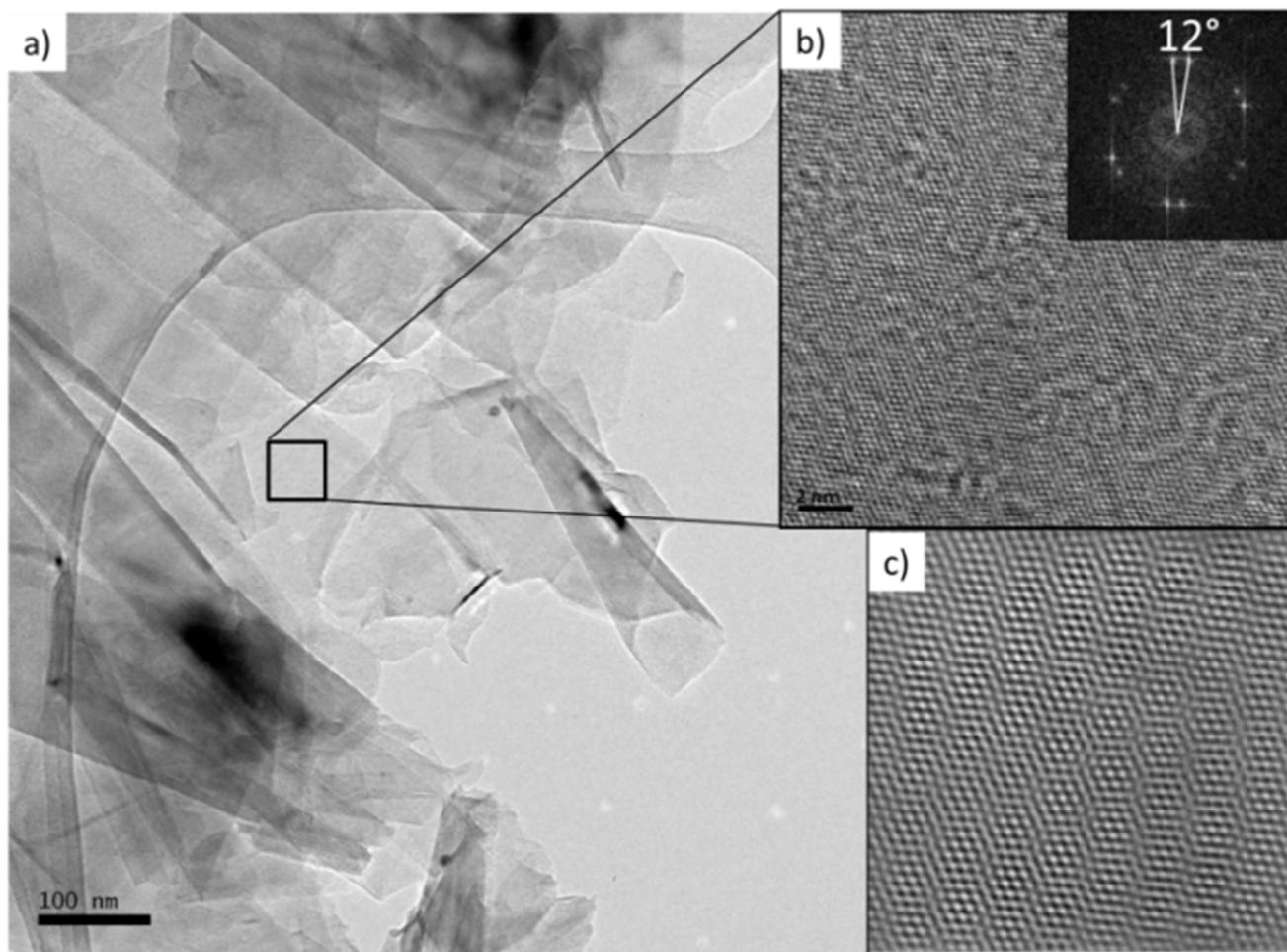


Figure 3: a) TEM image of wide sheet folded over itself; b) HRTEM image of a small area presenting an atomic-scale Moiré pattern. The inset FFT reveals a bilayer stacking with a relative rotational angle of  $12^\circ$ ; c) Reconstruction of the hexagonal atomic network from the FFT spot

## Conclusions

In this paper, we demonstrated that self-standing h-BN few-layers and monolayer can be easily obtained using the PDCs method. The use of lithium nitride ( $Li_3N$ ) as crystallization promoter allows to get highly crystallized  $sp^2$  boron nitride at relatively low temperature ( $1400^\circ C$ ) compared to standard methods. A simply ultrasonication process has been used to obtain nanostructures. One should note that the quantity and quality of BN sheets obtained this way, i.e.

thickness, area and organization are certainly affected by the sonication process and that the results presented here were obtained without any optimization. Further investigations on the exfoliation possibility are underway.

## Notes and references

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