Volume 13, Number 2, 2020. pp. 149-155

Jordan Journal of Physics

ARTICLE

From Amorphous Red Phosphorus to a Few Layers of Black Phosphorus: A Low-cost and Efficient Preparation Process

G. Tiouitchi[a,b], **F. ElManjli**[b,c], **O. Mounkachi**[a], **A. Mahmoud**[d], **F. Boschini**[e], **A. Kara**[e], **H. Oughaddou**[f,g], **M. Hamedoun**[b], **A. Benyoussef**[b,h] and **M. Ait Ali**[c]

[a] *LaMCScI, B.P. 1014, Faculty of Science-Mohammed V University, Rabat, Morocco.*

[b] *Materials and Nanomaterials Center, MAScIR Foundation, Rabat Design Center, Rue Mohamed Al Jazouli, Madinat Al Irfane, Rabat 10 100, Morocco.*

[c] *Coordination Chemistry Laboratory, Cadi Ayyad University, Faculty of Sciences Semlalia (UCA-FSSM), B.P. 2390 - 40000 Marrakech, Morocco.*

[d] *Greenmat, Cesam, Institute of Chemistry B6, University of Liege, 4000 Liège, Belgium.*

[e] *Department of Physics, University of Central Florida, Orlando, Florida 32816, USA.*

[f] *Institut des Sciences Moléculaires d'Orsay, ISMO-CNRS, Bât. 210, Université Paris-Sud, 91405 Orsay, France.*

[g] *Département de Physique, Université de Cergy-Pontoise, 95031 Cergy-Pontoise Cedex, France.*

[h] *Hassan II Academy of Science and Technology, Rabat, Morocco.*

Doi : https://doi.org/10.47011/13.2.6

Received on: 08/08/2019; *Accepted on: 16/12/2019*

Abstract: In this work, we present an efficiency synthesis method of phosphorene from red phosphorus by means of black phosphorus. The latter was synthesized by using copper, tin, tin iodide and red phosphorus as precursor at low pressure-temperature. Characterizations with powder X-ray diffraction, scanning electron microscopy (SEM), energy dispersive spectrometry (EDX), high-resolution TEM (HR-TEM) and Raman spectroscopy were performed to confirm the high quality and purity of black phosphorus crystal. Liquid phase method was used to exfoliate black phosphorus to phosphorene in N-methyl-2-pyrrolidone (NMP) as solvent. Atomic force microscopy and STEM were used to confirm the exfoliation of black phophorus in a few layers of phophorene.

Keywords: 2D materials, Red phosphorus, Black phosphorus, Phosphorene, Liquid-phase exfoliation.

Introduction

Black phosphorus (BP), the most stable form of phosphorus, is a 2D material expected to have potential applications [1], such as in nanocomposites [2], photovoltaics [3] and batteries [4]. While graphene (the 2D derivative of graphite) suffers from zero band gap [5] and molybdenite (MoS_2) suffers from the low mobility of its charge carriers [6], BP presents itself as a very promising material for the electronics and energy market, due to its high mobility of charge and direct gap (from 0.3 to 1.5 eV as a function of its thickness) [7]. Black phosphorus can be prepared by several methods, such as high-pressure synthesis [8,9], recrystallization from Bi [10,11] or Hg [12] and melting and annealing sequence at high temperatures [12,13]. All these methods often lead to small crystals with limited crystallinity, take a long time and in some cases even involve

Corresponding Author: M. Ait Ali **Email**: aitali@uca.ac.ma

toxic chemicals. In 2007, S. Lange et al. [14] synthesized black phosphorus from red phosphorus at low pressure and 873 K by adding small quantities of Au-catalyst, tin and tin (IV) iodide in a silica tube sealed under vacuum. This method produces several secondary phases in the final product, difficult to be eliminated. Thus, the development of a safe and simple method allowing to obtain black phosphorus with high crystallinity remains one of the present challenges preventing the use of black phosphorus and phosphorene for industrial applications. We have recently developed a modified method based on the choice of a cheap, abundant and non-toxic catalyst (Cu) to synthesize black phosphorus with high quality [15]. The main objective of the present work is the optimization of BP synthesis conditions using copper as catalyst and its liquid exfoliation in N-methyl-2-pyrrolidone (NMP) to produce dispersible BP flakes with controllable size and thickness, as well as in high yield.

Experimental

Black phosphorus was synthesized from amorphous red phosphorus (RP) by using Cu, Sn and SnI_4. The mineralizing SnI_4 was synthesized by adding 0.5g of Sn (Chempur, 99.999%) and 2.0g of I_2 (Chempur, 99.8%) to a solution of 25 mL of glacial acetic acid and 25 ml of acetic anhydride. The suspension was heated to reflux until the solution turned orange, indicating the completion of the reaction. After cooling, the crude product, crystallized as an orange solid, was filtered and further purified by recrystallization in hot chloroform. Black phosphorus was prepared as follows: Cu (22.7mg), Sn (42.5mg), red phosphorus (155.2mg) and SnI4 (10.0 mg) (molar ratio 1:1:14:0.045) were transferred into a silica glass ampoule, 10 cm in length, with an inner diameter of 1.0 cm and a wall thickness of 0.25 cm. The ampoule was sealed under vacuum placed horizontally in an oven and heated at 923K for 4 hours. The solid mixture was located in the hot end of the oven. The reaction was cooled to RT over a period of 72 hours with a slow rate of 0.2°C/min, which allows for better crystal growth. The product is formed in the cold section of the ampoule. The excess of SnI4 was removed by refluxing the mixture in toluene several times until the toluene remains clear (ultrasonic bath 20–45 min). No traces of other elements were observed in the final product.

The free layers of black phosphorus (i.e., phosphorene) were obtained by liquid-phase exfoliation (LPE) method [16,17]. Black phosphorus was exfoliated in N-methyl-2-pyrrolidone (NMP) (1mg/ml) using a bath ultrasonication (VWR - USC 600 THD (45 Hz)) for 8 hours. Similar to mechanical exfoliation, liquid-phase exfoliation cannot produce 2D materials with uniform size and thickness. To get layers with uniform size and thickness, an additional centrifugation step is required. For each speed of centrifugation, the supernatant was then further centrifuged at a high speed up to 13000 rpm (MC Medline 20000). The crystalline structure of the synthesized samples was analyzed by powder X-ray diffraction (D8 Discover Bruker AXS diffractometer, CuKα radiation, λ =1.540 Å). The microstructure and chemical composition of the prepared black phosphorus were studied using a high-resolution scanning electron microscope (Zeiss Ultra Plus, Zeiss, Germany) equipped with an energy dispersive x-ray spectrometer (INCA, Oxford, UK) and a scanning electron microscope (FEI, Quanta FEG 450) equipped with an EDX detector (BRUKER). Raman spectroscopy was carried out at room temperature using a confocal Labram 300 spectometer (Horiba Jobin-Yvon) and λ=532 nm and acquired on different locations of the sample powder. Aberration-corrected STEM analysis was carried out on a Jeol 2100F microscope operating at 200 kV. The size distribution was determined using a Zetasizer Nano ZS (Malvern Instruments, Ltd., UK) at 25 °C and atomic force microscopy (AFM) imaging was performed by using the Veeco Dimension ICON system operating in tapping mode.

Results and Discussion

The optimization of the quantity of copper used as catalyst for the synthesis of BP was studied. The three tests were realized using the same procedure announced above and the products of the recovered tubes are then analyzed (cold zone and hot zone).

The diffractograms of the obtained phases during the optimization tests are represented in Fig. 1(a-e) according to the following nomenclature in Table 1.

Analysis of the phases recovered in the tubes revealed the compositions grouped in Table 2.

TABLE 1. Nominations used in the phase analysis.

Abbreviation	Signification
BP2QZF	Products recovered in the cold zone of the tube (synthesized with Cu 2Q) 2Q = 45.5 mg.
BP2QZC	Products recovered in the hot zone of the tube (synthesized with Cu 2Q).
BP1QZF	Products recovered in the cold zone of the tube (synthesized with Cu 1Q) 1Q = 22.75 mg.
BP1QZC	Products recovered in the hot zone of the tube (synthesized with Cu 1Q).
BP1QZC	Products recovered in the hot zone of the tube (synthesized with Cu 1/2Q) 1/Q = 11.37 mg.

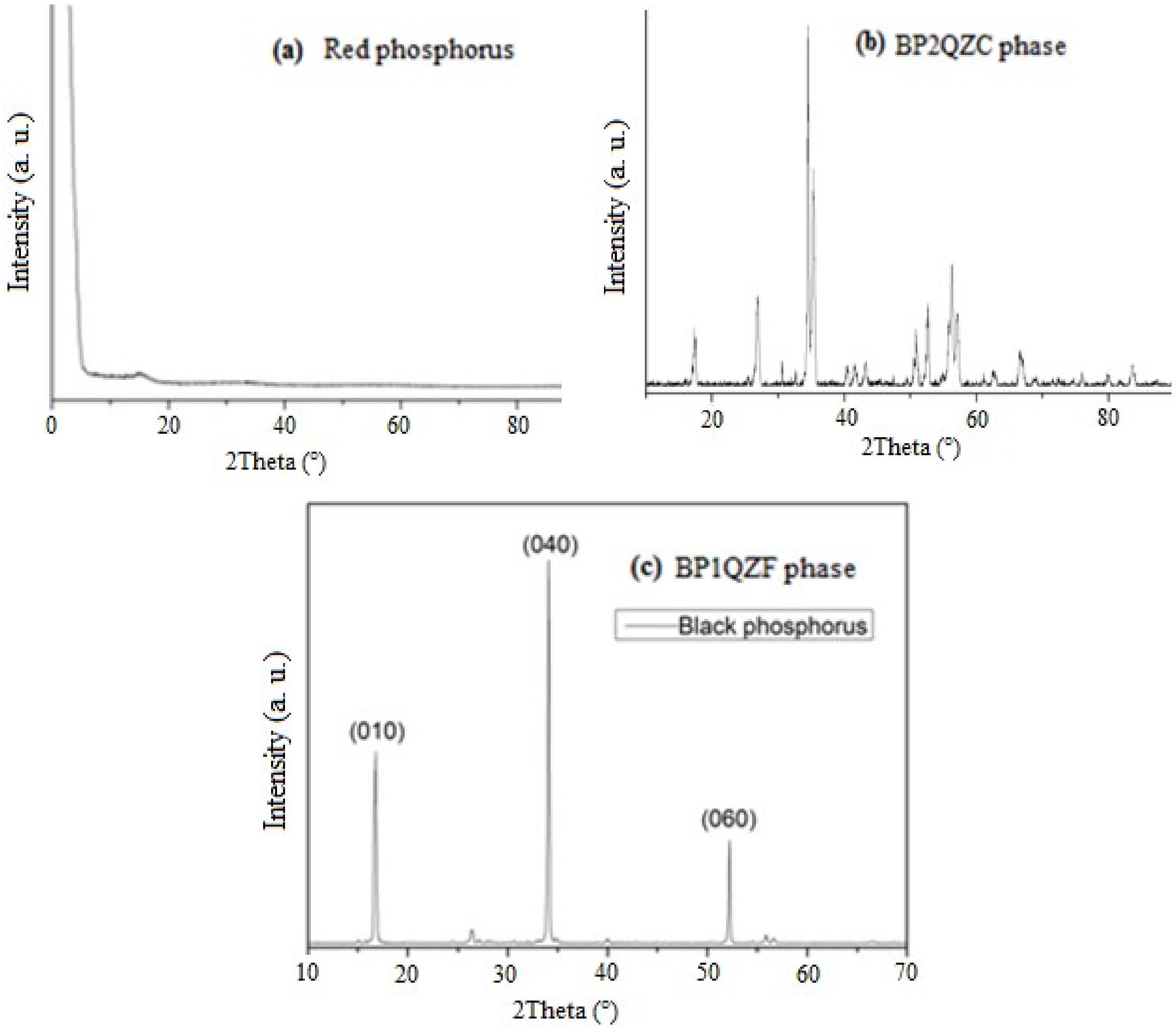


FIG. 1. X-ray powder diffraction: a) red phosphorus, b) BP2QZC phase and c) BP1QZF phase.

TABLE 2. Influence of the amount of Cu in the synthesis of black phosphorus.

Amount of Cu	Phases in the hot zone	Phases in the cold zone	Remarks
22.75 mg	Cu_4SnP_{10} Cu_2P_7 $SnCu_2P_2$ Cu P_2O_5 PO_2	Black phosphorus (BP)	• High crystallinity of black phosphorus • Traces of oxygen in the tubes
45.5 mg	Cu_2P_7 Cu_4SnP_{10} SnI_4	Black phosphorus (BP) Iodine SnI_4 SnP_3 CuSn	• Low crystallinity • a, b, c different from those of 1 Q • SnI4 appeared, because washing is not performed.
11.37 mg	Amorphous RP Cu SnI_4	RP spread on the surface of the tube	• The amount of Cu is insufficient to convert RP into BP.

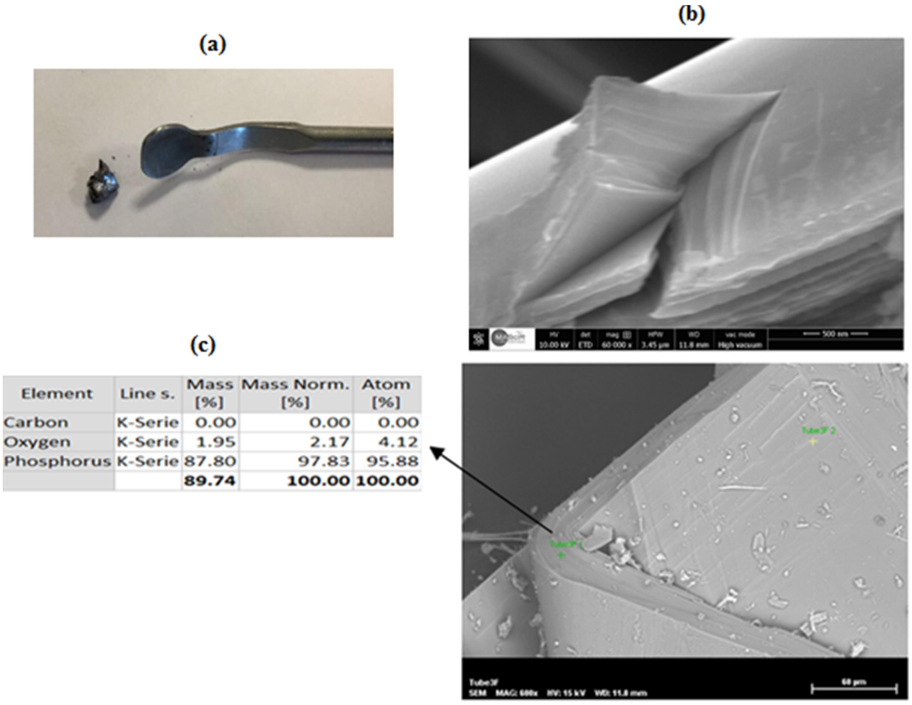
The existence of traces of oxygen in the tubes led to the existence of secondary phases composed by the starting materials. The optimal amount of Cu to produce black phosphorus with good crystallinity and purity was 22.75mg. The tests with 11.37mg of copper did not make it possible to obtain black phosphorus; the quantity of Cu could not convert red phosphorus into black phosphorus. The tube analysis showed the existence of black phosphorus spread on the surface of the tube in the hot zone and in the cold zone.

The XRD pattern of the obtained black phosphorus using 22.75mg of copper is presented in Fig 1.c and shows the presence of only three peaks corresponding to the planes (020), (040) and (060), indicating a pure and well-crystallized BP material according to the BP (PDF: 04-015-0991), space group Cmce (No: 64). The X-ray data demonstrates the high purity and crystallinity of BP without impurities. The strong preferential orientation along the b-axis is observed by analyzing the (040) diffraction peak. The obtained lattice parameters are a = 3.314 Å, b = 10.482 Å and c = 4.375 Å.

Typical SEM micrographs and EDX spectra of the obtained black phosphorus are shown in Fig.2. The SEM pictures clearly show the layer architecture of black phosphorus. A semi-quantitative EDX measurement is used to determine the chemical composition of the crystal, revealing a composition of P (97.83wt %) and O_2 (2.17wt %). The detected oxygen can be attributed to the exposure of black phosphorus to air during handling and characterization.

The identification of the vibrational mode of black phosphorus was found to be in agreement with the studies reported in the literature [18,19]. In the low-frequency region, we observe a mode with medium to low intensities. As shown in Fig. 3, three Raman peaks are observed at 362.5 cm^{-1}, 438.6 cm^{-1} and 467.5 cm^{-1}, corresponding to A^{1}g, B^{2}g and A^{2}g normal vibrational modes (Fig. 3a, 3b), which are in good agreement with the reported data on black phosphorus in literature. These results are consistent with the XRD data and confirm the high purity of the prepared BP.

Transmission electron microscopy (TEM) analysis of the as-synthesized BP is shown in Fig. 4. Large crystalline grains with a size of about 6×15 µm² are observed (Fig. 4a), where single crystallinity is shown in the high resolution which is an important request for electronic applications. A careful measurement of the lattice fringes in the HR image (Fig. 4b) gives a value of around 2.3 Å that corresponds to the (014) planes of a bulk BP crystal, which is coherent with well-known BP lattice parameters.



Element	Line s.	Mass [%]	Mass Norm. [%]	Atom [%]
Carbon	K-Serie	0.00	0.00	0.00
Oxygen	K-Serie	1.95	2.17	4.12
Phosphorus	K-Serie	87.80	97.83	95.88
		89.74	**100.00**	**100.00**

FIG. 2. (a) Photograph of black phosphorus, (b) SEM images of black phosphorus and (c) EDX measurements.

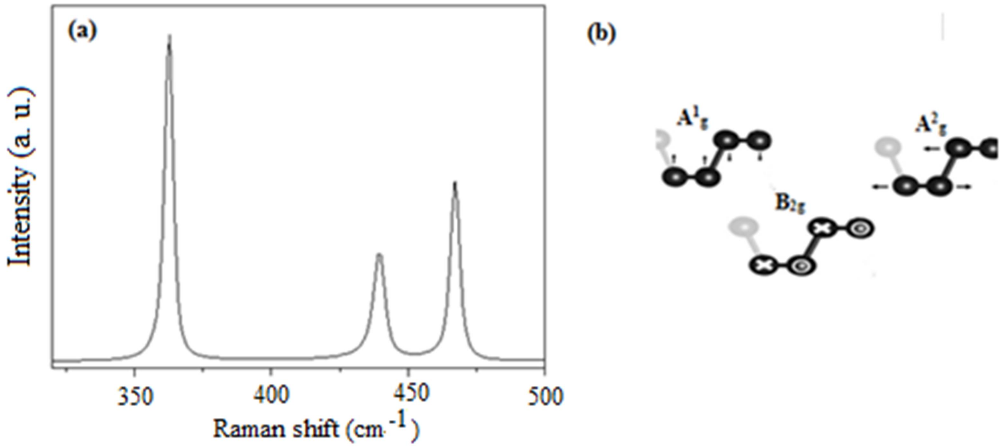


FIG. 3. (a) Raman spectrum of as-prepared black phosphorus recorded at room temperature and (b) vibrational modes of black phosphorus.

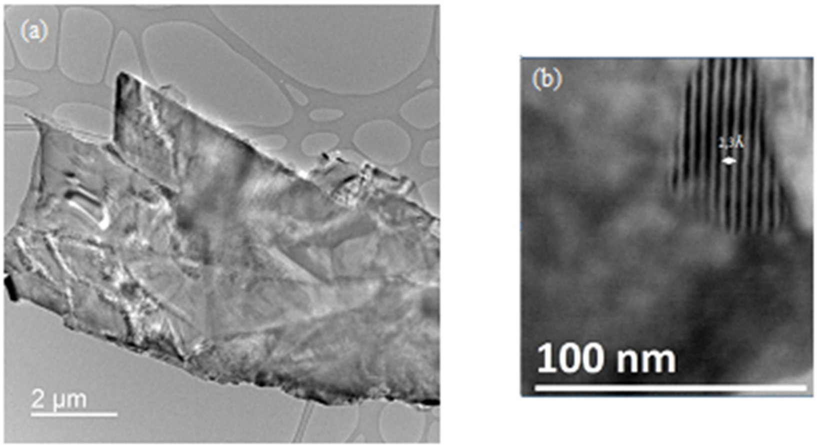


FIG. 4. (a) TEM analysis of black phosphorus and (b) corresponding lattice fringes.

Liquid exfoliation of the prepared black phosphorus in NMP gave a dispersed supernatant which was centrifuged at 13000 rpm. STEM analysis (Fig. 5) shows the dispersion of the nanosheets, which approves the success of BP exfoliation.

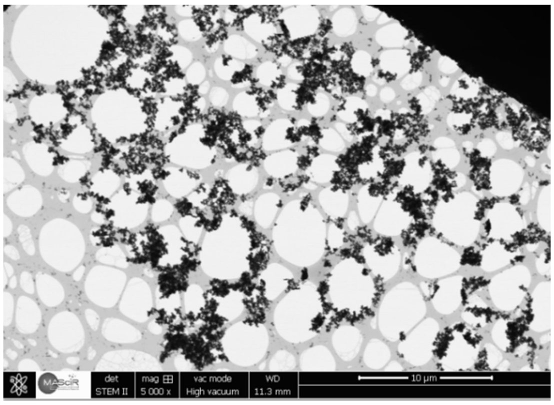


FIG. 5. STEM analysis of exfoliated black phosphorus (13000 rpm).

AFM experiments revealed the presence of layers with a narrow range of shapes and sizes. Height profiles taken on large nanosheets revealed a thickness of about 23 nm (Fig. 6). Previous AFM measurements in the literature [20] suggest that single-layer phosphorene has a thickness of 0.9 nm. Therefore, AFM images here suggest that the large nanosheets consist of 18-20 phosphorene layers. However, single- or bilayer phosphorene (0.9-1.6 nm) thickness can be produced by improving the experimental conditions (sonification power and time, centrifugation speed, … etc.). The AFM results suggest that increasing the exfoliation time for more than 8 hours breaks down the larger sheets into smaller nanosheets that could be predominantly single- and bilayer phosphorene. We have shown by this exfoliation that our synthetic product is easily exfoliable and could potentially give high-quality systems with controlled number of layers.

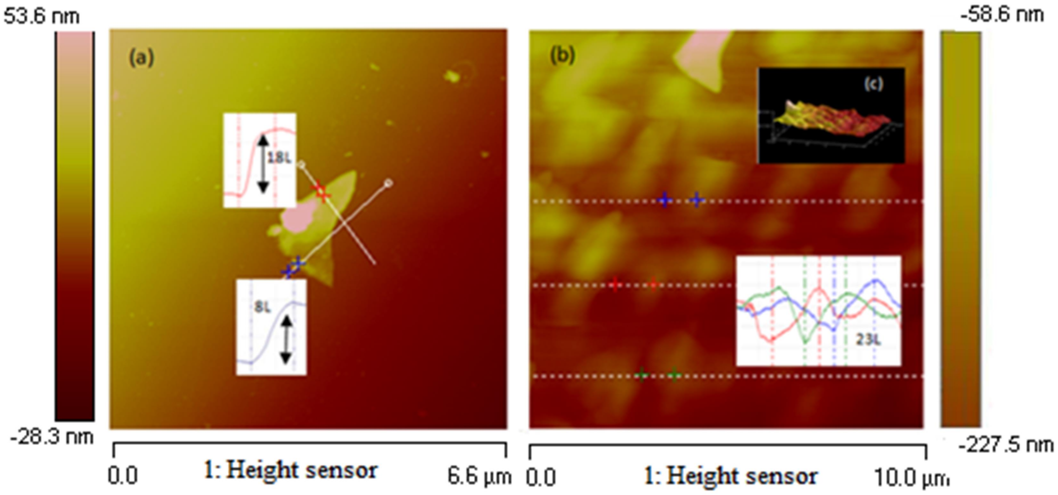


FIG. 6. AFM image of exfoliated BP layers deposited on SiO_2/Si a) lower concentration of BP in NMP (1mg/ml), b) higher concentration (5mg/ml) and c) three-dimensional representation of the surface in (c).

Conclusion

In this paper, we have improved the conditions of synthesis of black phosphorus with high yield and quality. This method also reduces phases that appear with gold as catalyst, which are sometimes difficult to remove. The presence of some traces of SnI_4 on the final product can be eliminated by washing with toluene. The crystal quality is proved by X-ray, Raman and SEM. The crystal with sizes in the order of several millimeters can be exfoliated easily (8h-sonification followed by centrifugation) into one or more layers depending on the speed of centrifugation and the solvent used. These layers of phosphorene are interesting for various applications in microelectronics and photo catalysis.

References

[1] Samuel Reich, E., Nature, 506 (2014) 19.

[2] Tiouitchi, G., Raji, M., Mounkachi, O., Ait Ali, M., Mahmoud, A., Boschini, F., Essabir, H., Bouhfid, R. and El Kacem Qaiss, A., Compos., Part B: Eng., 175 (2019) 107165.

[3] Buscema, M., Groenendijk, D.J., Steele, G.A., van der Zant, H.S.J. and Castellanos-Gomez, A., Nat. Commun., 5 (2014) 4651.

[4] Park, C.-M. and Sohn, H.-J., Adv. Mater., 19 (2007) 2465.

[5] Gui, G., Morgan, D., Booske, J., Zhong, J. and Ma, Z., Appl. Phys. Lett., 106 (2015), DOI 10.1063/1.4907410.

[6] Fivaz, R. and Mooser, E., Phys. Rev., 163 (1967) 743.

[7] Tran, V., Soklaski, R., Liang, Y. and Yang, L., Phys. Rev. B, 89 (2014) 235319.

[8] Shirotani, I., Mol. Cryst. Liq. Cryst., 86 (1982) 203.

[9] Jamieson, J.C., Science, 139 (1963) 1291.

[10] Bridgman, P.W., J. Am. Chem. Soc., 36 (1914) 1344.

[11] Maruyama, Y., Suzuki, S., Kobayashi, K. and Tanuma, S., Phys. B+C, 105 (1981) 99.

[12] Krebs, H., Weitz, H. and Worms, K.H., ZAAC J. Inorg. Gen. Chem., 280 (1955) 119.

[13] Baillargeon, J.N., Cheng, K.-Y., Cho, A.Y., Chu, S.-N., Chu, G. and Hwang, W.-Y., Lucent Technol. Inc., Murray Hill, N.J., Assignee, (2000) 2.

[14] Lange, S., Schmidt, P. and Nilges, T., Inorg. Chem., 46 (2007) 4028.

[15] Tiouitchi, G., Ait Ali, M., Benyoussef, A., Hamedoun, M., Lachgar, A., Benaissa, M., Kara, A., Ennaoui, A., Mahmoud, A., Boschini, F., Oughaddou, H., El Kenz, A. and Mounkachi, O., Mater. Lett., 236 (2019) 56.

[16] Backes, C., Higgins, T.M., Kelly, A., Boland, C., Harvey, A., Hanlon, D. and Coleman, J.N., Chem. Mater., 29 (2017) 243.

[17] Brent, J.R., Savjani, N., Lewis, E.A., Haigh, S.J., Lewis, D.J. and O'Brien, P., Chem. Commun., 50 (2014) 13338.

[18] Sugai, S., Ueda, T. and Murase, K., J. Phys. Soc. Japan, 50 (1981) 3356.

[19] Vanderborgh, C.A. and Schiferl, D., Phys. Rev. B, 40 (1989) 9595.

[20] Liu, H., Neal, A.T., Zhu, Z., Luo, Z., Xu, X., Tománek, D. and Ye, P.D., ACS Nano, 8 (2014) 4033.