Playing with temperature in the synthesis of nitrogen rich carbon nanothreads

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Keywords: nitrogen carbides, induced polymerization, nanothreads, kinetics

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Carbon nanothreads are one-dimensional sp^3 carbon nanomaterial produced in non-topochemical reactions under unidirectional stress of simple aromatics. Pressures in excess of 20 GPa have been employed to synthesize these attracting materials with "cage-like" structures consisting of fused cyclohexane rings arranged in complex structures and geometries [1-3]. These materials can combine properties like flexibility, strength and resilience representing a sort of diamond wires. The first syntheses were performed compressing benzene both in diamond anvil (DAC) and Paris-Edinburgh cells [4,5], The threads were parallel arranged along the c-axis of hexagonal crystals spaced by 6.5 Å while the spacing between the (100) planes was 5.6 Å. After that, other nitrogen rich nanothreads have been synthesized by aniline [6] and pyridine [7], while many others have been predicted [8]. The nanothreads obtained by pyridine and aniline are rather different. In fact, while the material obtained by pyridine is a sort of carbon nitride where nitrogen substitute carbon atoms, in that resulting from the compression of aniline the amino groups do not participate to the reaction decorating the exterior of these nanothreads. In this way, they can act as preferential active sites for doping, and as linkers for molecules with biological interest and inorganic nanostructures.

The high pressures necessary to drive the reaction and the low reaction yield represent the main limits to the exploitation of this synthetic method. Temperature is expected to play an important role in modifying the pressure conditions for the nanothreads formation. A temperature increase should favor the lowering of the pressure onset of the transformation thanks to the increase of the amplitude of the lattice motions and of the consequent exploration of different intermolecular conformations but, on the other side, it could also reduce the stress directionality and consequently the selectivity to the nanothreads formation. A low temperature compression could instead magnify the efficiency of the stress directionality bringing to a yield increase. Here we discuss recent findings on the reactivity of aniline and pyridine under high pressure and variable temperature conditions.

[1] *E. S. Xu, P. E. Lammert, V. Crespi, Nano Lett. 2015, **15**, 5124.*
[2] *B. Chen, R. Hoffmann, N. W. Ashcroft, J. Badding, E. S. Xu, V. Crespi, J. Am. Chem. Soc. 2015, **137**, 14373.*
[3] *F. Yang, Y. Lin, M. Baldini, J. E. P. Dahl, R. M. K. Carlson and W. L. Mao, J. Phys. Chem. Lett., 2016, **7**, 4641.*
[4] *T. C. Fitzgibbons et al. Nat. Mater. 2015, **14**, 43.*
[5] *X. Li et al. J. Am. Chem. Soc. 2017, **139**, 16343.*
[6] *M. M. Nobrega, E. Teixeira-Neto, A. B. Cairns, M. L. A. Temperini and R. Bini Chem. Sci., 2018, **9**, 254.*
[7] *X. Li et al. J. Am. Chem. Soc., **2018**, 140, 4969.*
[8] *J. F. R. V. Silveira and A. R. Muniz, Phys. Chem. Chem. Phys., 2017, **19**, 7132.*