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Unveiling the metallic impurities in detonation nanodiamond by a total oxidation treatment

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The first artificial nanodiamonds were produced in the 1960s by USSR scientists using a detonation process. In the late 1990s, there was a growing interest in this material since detonation nanodiamonds (DNDs) became available at a large scale. NDs inherit most of their properties of the bulk, such as strong hardness, high thermal conductivity and electrical resistivity, as well as interesting optical properties and fluorescence. NDs are also biocompatible, leading to a large field of possibilities for biomedical applications. The surface of NDs is also highly reactive, thus allowing drug-delivery applications. Nowadays, NDs have high potential in neutronics for slow neutron reflectors [1], magnetic resonance imaging, tribology and lubrication, nanofluids, and in biomedical (cancer treatment, drug delivery, etc.) [2,3].

However, detonation and purification processes of NDs produce a non-negligible amount of impurities. The sp² carbon layer at their surface, the presence of surface functional groups (-OH, -COOH, -CO, etc.) and metallic impurities are especially unfavorable for neutron applications because of their high neutron absorption [1]. Metallic impurities, which can act as “Trojan horses” are undesirable in biomedical applications since they cause more harms than goods. A universal method producing pure NDs does not exist so far; therefore all the DNDs in the industry are different, with a variable amount of impurities [4]. Thus, there is a real need to understand the composition of DNDs in order to obtain high purity DNDs. Adding the fact that the metallic impurities can be present at a content of 1-2 wt.% in the commercial DNDs, without knowing their specific localization (on the surface or within ND clusters), most of the characterization techniques reach their limits of detection (LOD) making impurity identification complicated. The use of sensitive but standard techniques (contrary to Neutron or Prompt-Gamma Activation Analysis and high-resolution ICP-MS) is of urgent need to fully exploit commercial DNDs for the promising applications [1,5].

In this paper, we propose to apply highly selective methods to efficiently purify DNDs. Halogen chemistry has the potential to fully match the requirements of the development of a scalable approach to produce high-purity DNDs. One-pot straightforward gaseous thermal treatments based on chlorine and fluorine gases are shown to selectively remove the metallic impurities and the surface functional groups, respectively with high removal yield. Moreover, with the purpose of filling the gap of understanding of DNDs, we propose an unprecedented method to determine the nature of their metallic impurity inclusions. Total oxidation of DNDs is simply carried out leading to consumption of the carbon species and revealing the remaining impurities in an oxidized state (Me-O) in a highly concentrated state. In order to characterize these impurities in NDs and Me-O, standard techniques have been used, such as Thermogravimetric Analysis, Powder X-Ray Diffraction, X-ray photoelectron spectrometry, Mössbauer, infrared and Raman spectroscopies, as well as Scanning and Transmission Electron Microscopy analyses. The approach proposed here could become a universal process to concentrate the metallic impurities contained in any kind of carbon nanomaterial sample, offering that way a reliable tool overcoming the LOD of all standard characterization techniques for detection and quantification of metal-based impurities.

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