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A comprehensive study of the effect of thermally induced surface terminations on nanodiamonds electrical properties

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ABSTRACT

Nanodiamonds (NDs) gained increasing attention in multiple research areas due to the possibility of tuning their physical and chemical features by functionalizing their surface. This has a crucial impact on their electrical properties, which are essential in applications such as the development of innovative sensors and in the biomedical field. The great interest in electrical conduction in NDs has driven the scientific community to its extensive investigation. The role of various functionalities has been considered and different conduction mechanisms have been proposed. In this work, we reported on a systematic study of the modification of the electrical properties of differently sized NDs, as a function of different thermal treatments in air, hydrogen or inert atmosphere. Samples were electrically characterized in controlled humidity conditions to consider the influence of water on conductivity. NDs electrical properties were interpreted in connection with their surface chemistry and structural features, probed with infrared and Raman spectroscopies. The presence of surface graphite, hydrogen terminations or water adsorbed on hydrophilic oxygen-containing functional groups rendered NDs more conductive. These moieties indeed enabled different conduction mechanisms, which were respectively graphite-mediated conduction, water-induced transfer doping and Grotthus mechanism in surface-adsorbed water. The effect of particles size on conductivity has also been evaluated and discussed. Our experimental findings shed light on the link between surface modifications and electrical properties of NDs, providing at the same time an interpretative key to understanding the effect of particles dimensions.

1. Introduction

Due to their appealing properties, including extreme hardness, high thermal conductivity, presence of photoluminescent defects [1–5] and excellent biocompatibility, nanodiamonds (NDs) are currently studied in a wide variety of research fields. These encompass tribology [6–8], catalysis [9–12], energy storage and conversion [13–15], photonics [16–18], quantum sensing [19–24] and biomedical applications [25–27]. These nanocrystals, whose size spans from few nm up to 300 nm, are typically obtained from detonation of carbon-containing explosives [28,29] or from milling of High-Pressure-High-Temperature (HPHT) microdiamond powders [30]. Nonetheless, other production techniques can be exploited as well, as for instance Chemical Vapor Deposition (CVD) [31], laser ablation [32], high-energy ion irradiation of graphite [33] and synthesis from molecular precursors [34,35].

NDs typically exhibit a peculiar core-shell structure made up of a diamond core, a middle layer constituted by distorted sp^3 phases and amorphous carbon, and an outer shell formed by sp^3 and sp^2 carbon atoms with dangling bonds terminated by various moieties [36]. These surface functionalities are typically oxygen-containing species in as-synthesized NDs (*e.g.*, carbonyls, carboxyls, ethers, acid anhydrides and alcohol functions). However, surface groups can be easily tailored

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