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Synthesis and characterization of porphyrin functionalized nanodiamonds

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ABSTRACT

We report on a novel synthetic pathway for the chemical functionalization of nanodiamonds with porphyrin. To this scope, the NDs, after a thermal treatment essential to organize the crystal surface, were derivatized with reactive moieties useful to conjugate the ND with porphyrin. Untreated and modified nanoparticles were systematically characterized by X-ray photoelectron, Raman, photoluminescence and infrared spectroscopies with the purpose of evaluating the effects due to the crystals manipulation and confirming the efficacy of the proposed approach. An investigation of the effects induced to the samples by laser irradiation (probe for Raman and PL spectroscopies) was performed, highlighting the significant increase of temperature that is associated to the redshift of Raman diamond peak.

1. Introduction

In the last decades, innovative biological probes based on the unique optical and chemical properties of nanoscale materials were produced. Particularly, the employment of nanoparticles has been investigated in different environments, offering promising perspectives in biomedical research, diagnostics and therapy [1–5]. One of the most interesting materials in this context is diamond, which has received an increasing attention thanks to its very low toxicity and bio-compatibility. Furthermore, it has extremely high chemical inertness and structural stability in biological environments [6,7]. Complementarily to the above-mentioned general chemical inertness, the surface of diamond nanoparticles can be chemically decorated with a variety of functional molecules employing several different chemical processes (i.e. Diels-Alder reaction [8,9]). This opportunity is offered by the different surface termination groups that can be attached after the particle synthesis or due to specific treatments [10,11].

Nanodiamonds (NDs) derived from the fragmentation of samples produced with high-pressure high-temperature (HTHP) synthesis are characterized by a low fraction of sp^2 carbon on their surface, with respect to other synthetic methods such as detonation [12].

These nanoparticles could be used in the preparation of new sensitizer for photodynamic (PDT) or sonodynamic therapy (SDT) applications, which represent innovative approaches to treat cancer [13,14]. Both techniques are based on a similar molecular mechanism [15], which involves either the sensitizer excitation (by light in PDT, or by ultrasound – via acoustic cavitation – in SDT) followed by reactive oxygen species (ROS) production, or by interaction with oxygen during the decay time. The produced sono/photodynamic ROS are cytotoxic and they are responsible for cells death.

Porphyrin molecules possess such physical-chemical features to be considered the first generation of sensitizers [16,17]. They are non-toxic to cell cultures [18] if they are not exposed to external stimuli as ultrasounds or light irradiation. For those reasons, they are widely used as model compounds in photo- and sono-dynamic studies.

In this study, we conjugate a porphyrin molecule to nanodiamond surface in order to develop a new hybrid nanomaterial which can represent an interesting model for PDT and SDT applications.

2. Materials and methods

2.1. Sample fabrication

The sample under exam consists of a commercial dispersion of synthetic nanodiamond (Micron + MDA 0–0.25, ElementSix™) realized by means of grinding of High Pressure High Temperature (HPHT) single-crystals. The NDs are classified as type Ib, having a nominal concentration of single substitutional nitrogen comprised between 10 ppm and 100 ppm. The diamond nanoparticles size nominally ranges between a few nm and ~300 nm.

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