Biofunctionalization of annealed nanodiamonds

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Introduction
Due to their outstanding properties, nanodiamonds are a promising nanoscale material in various fields of applications such as microelectronics, polishing, optical monitoring, medicine, and biotechnology. Beyond the typical diamond characteristics like extreme hardness or high thermal conductivity, they have additional benefits like intrinsic fluorescence due to lattice distortion without photobleaching. Further the carbon surface and its various functional groups in consequence of the synthesis, facilitate additional chemical and biological modification. It is of particular interest in biological and medical applications, that toxicity has not been observed so far. This distinguishes nanodiamonds from other nano-sized carbon species like nanotubes, nanonions, or fullerenes and makes them to a powerful tool to improve biocompatibility [1].

Properties of nanodiamond

detonation nanodiamond (DND):
primary particle size 3 - 7 nm
primary aggregate size of 30-100 nm secondary agglomerates up to several micrometers large
after detonation synthesis, core of diamond and shell of graphitic carbon after purification the DND contain a variety of functional groups such as carboxylic acid groups, amine groups, alcohol groups, hydroxyl groups, and other functional groups.

(1) homogenization through carboxylation, activation via carbodiimide (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide - EDC) [chemicate]
(2) homogenization through thermal annealing at 900 °C, carboxylation, activation via thionyl chloride
(3) homogenization through thermal annealing at 1100 °C (surface graphitization), in situ generated diazonium salt through reaction of isopentylnitrile with O-phosphorylethanolamine leads to creation of C-C-bonding [5]

Characterization of modified nanodiamonds

FTIR transmission measurements:
- Thermo Scientific: Nicolet iZ10
- 32 scans, 4 cm⁻¹/resolution
- KBr pellet: 0.3 wt% sample in KBr
- thermal annealing leads to a reduction of functional groups at the nanodiamond surface
- at 900 °C still some residues recognizable
- at 1100 °C only little water residues of either KBr or during sample preparation

FTIR-ATR measurements:
- Bruker, ALPHA FTIR
- 32 scans, 4 cm⁻¹/resolution
- PEA peaks can be clearly identified in IR spectra for click chemistry (green graph)
- easy and suitable method for DND modification with phosphonate groups
- Y=C=O (COOH) recognizable for EDC and SOCl₂ activation, PEA peaks might be hidden under broad band

Conclusion and Perspectives
The authors realized a succesful modification of nanodiamond with phosphate groups. The most promising method is click chemistry at graphitized nanodiamond to create a new C-C-bonding between the sp shell and the O-phosphorylethanolamine. The next step will be the use of phosphorylated nanodiamonds for surface modification of titanium-based implants to increase their biocompatibility by integration of the DND in an anodically grown titanium oxide layer [8]

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