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 nanosized carbon species like nanotubes, nanoonions, or fullerenes and make them to a powerful tool to improve biocompatibilty .[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 DND contain a variety of functional groups [2,3]
- lattice effects due to synthesis enabling fluorescence
- color centers in the crystal show no or very low photobleaching [4]

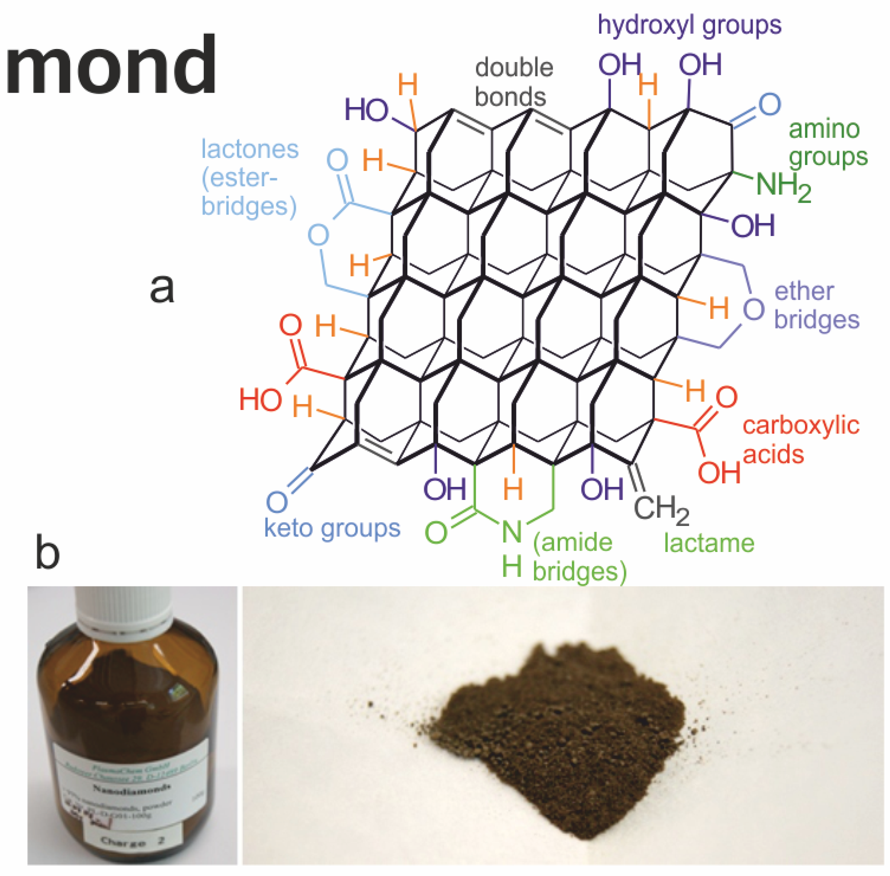


Fig. 1 (a) Schematic representation of DND's core and shell structure after detonation synthesis and purification (by J. Michael); (b) DND powder by Plasmachem

Thermal annealing of nanodiamond

conditions:

- starting material: DND (Plasmachem PL-D-G01)
- oven PEO603 from ATV
- heating rate 50 K/min
- duration of annealing 2 h
- cool down within 2 h
- 20 min nitrogen flow 14 l/min at room temperature
- 3 l/min during heating and cool down
- color of DND powder changed from grayish to black

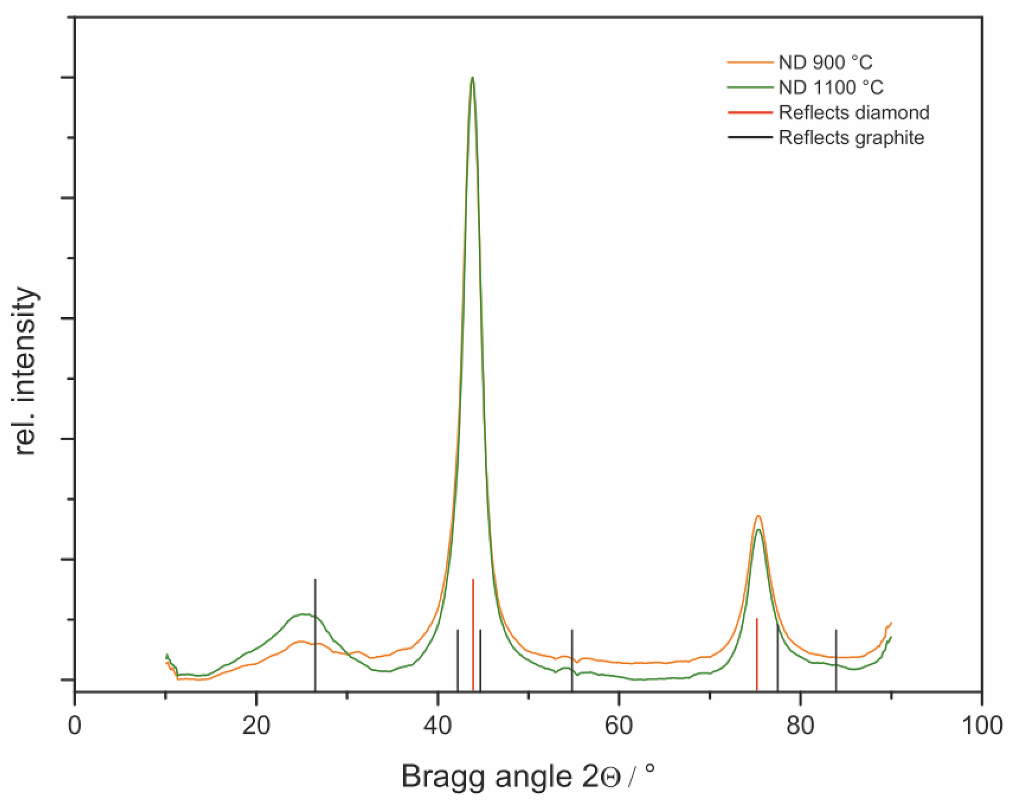
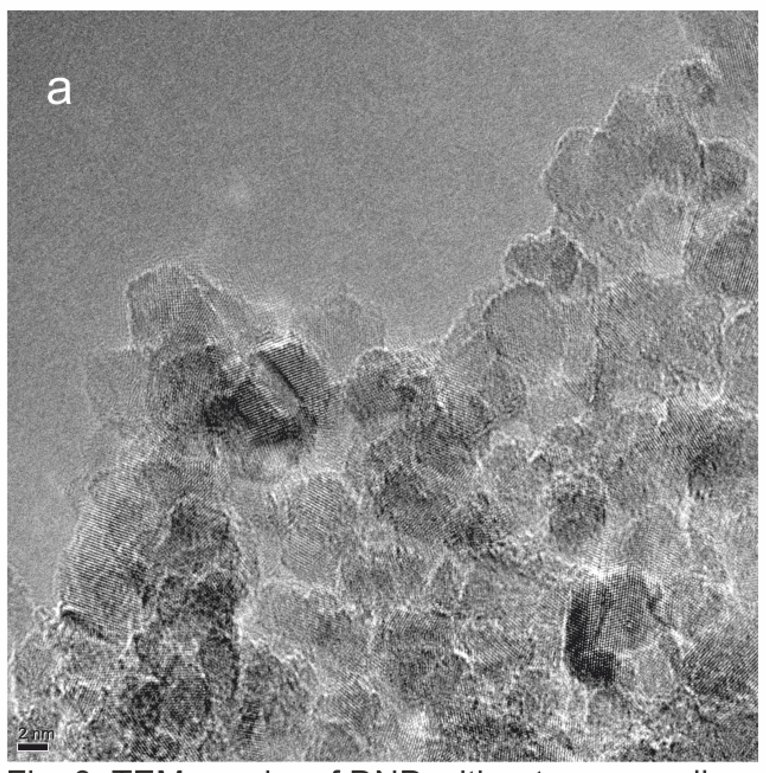


Fig. 2 X-Ray powder diffraction pattern of detonation nanodiamond annealed at 900 °C (orange graph) and 1100 °C (green graph) compared to calculated reflect positions of bulk diamond (red) and graphite (black).



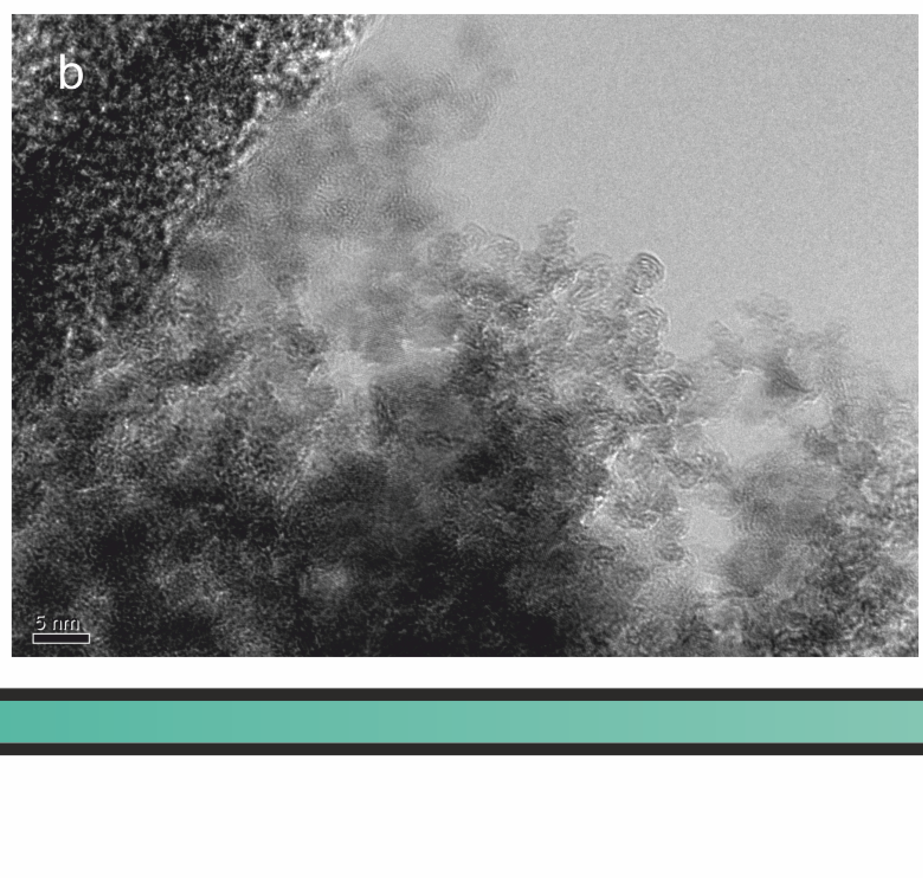
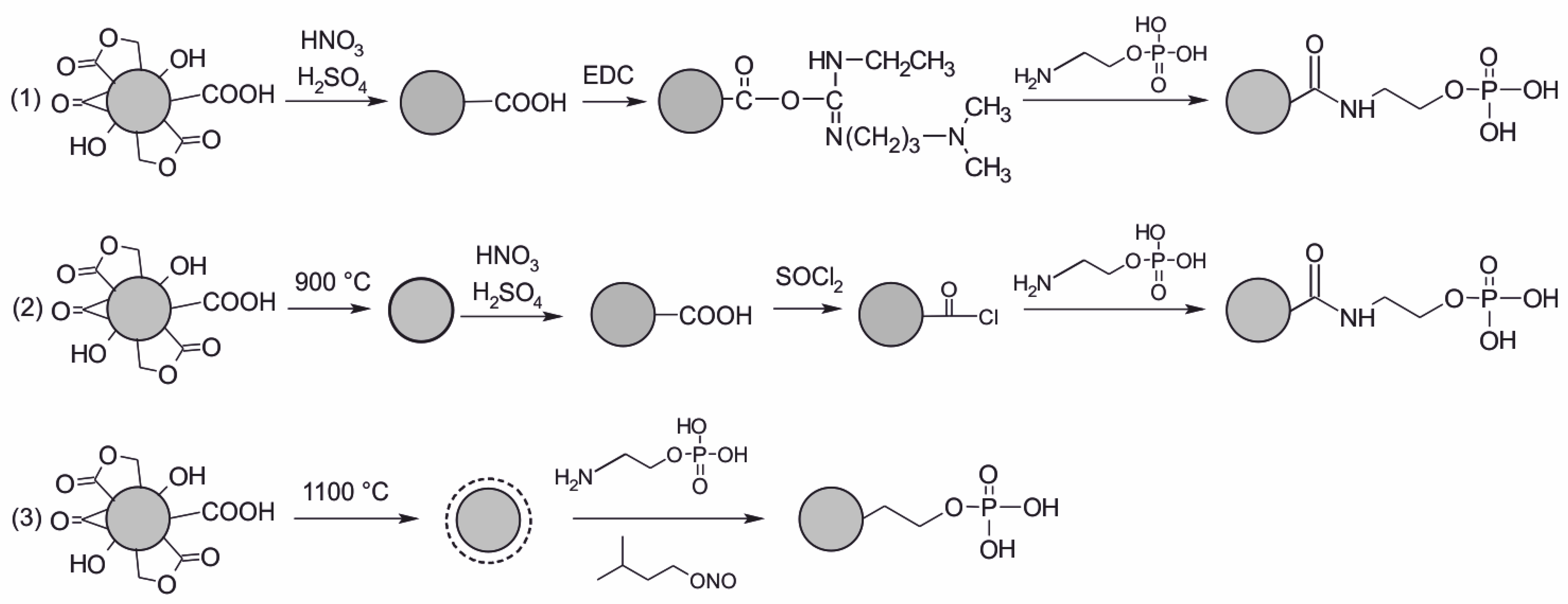


Fig. 3 TEM graphs of DND without annealing (a) and after annealing at 1100 °C (b). Change of crystal structure from sp^3 carbon (a) to onion structure of sp^2 carbon (b) can be observed, results match with XRD data.

Functionalization of nanodiamond

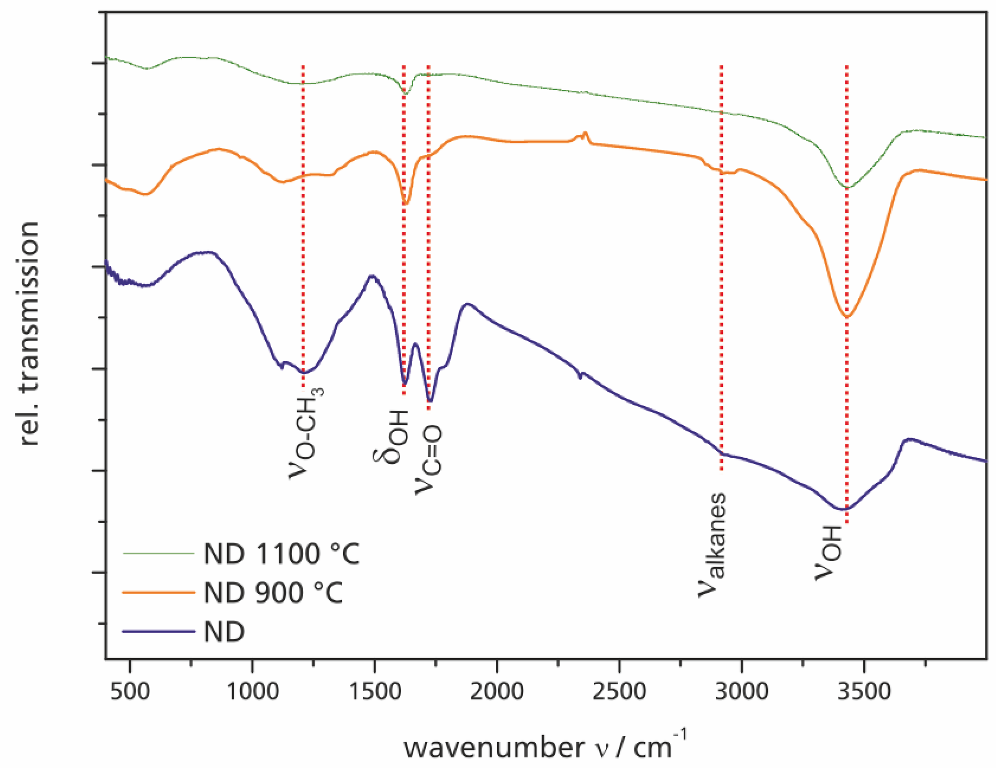


(1) homogenization through carboxylation, activation via carbodiimide (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide - EDC) [chemicell]

(2) homogenization through thermal annealing at 900 °C, carboxylation, activation via thionyl chloride

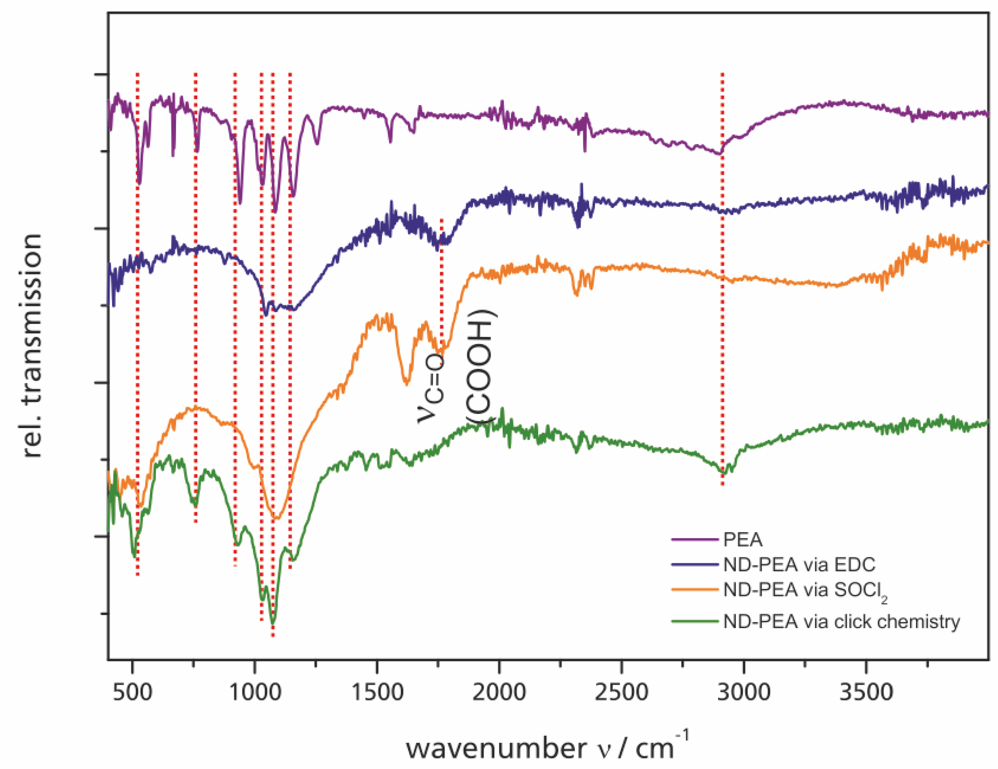
(3) homogenization through thermal annealing at 1100 °C (surface graphitization), *in situ* generated diazonium salt through reaction of isopentylnitrite with O-phosphorylethanolamine leads to creation of C-C-bonding [5]

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 phosphate groups
- $\nu_{C=O}$ (COOH) recognizable for EDC and $SOCl_2$ 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^2 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. [6]

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