WP2: Nanodiamonds

Research strategy and methodology

The main goal of the WP2 is to establish robust procedures for preparation of diamond nanoparticles with customized parameters (size, crystallinity, doping, level and type of defects). The research strategy thus comprises implementation of the detonation synthesis for preparation of nanodiamonds in high-yield and of high-purity corroborated by detailed analysis of the products in each step during the detonation and purification processes. Such approach based on availability of the experimental detonation chamber thus offers the possibility of step-by-step tuning and monitoring of the process, which intdoruces more flexibility when optimizing the whole technological procedure.

An entirely new input with respect to control of the detonation-induced reactions is to vary composition of the detonation batch by means of using different ratio of explosives, use of metal-free batches or admixing of elements, which are capable of advancing the properties of DNDs such as Si (testing possibility of formation of the Si-V centers) and transition metal elements ("luminescence shifters"). The overall concentration of defects and DND crystallinity will be also monitored and the conditions for preparation of DND particles with the specific structural properties will be established.

The purification process is partly based on already approved sequences. The obtained diamond soots (DS) will be first separated mechanically at large scale with assistance of acidic treatments. The separated DND agglomerates composed of a multishell diamond nanoparticles (shown in *Fig. 9 (i) and(ii))* will be subjected to further heating and acidic treatments (HCl, HF) in order to induce weakening of the hardness of the primary agglomerates. The decoupled DND articles will be subjected to other purification steps using acidic treatments (HNO_3, $KMnO_4/HNO_3$, HCl etc.) and complex agents (EDTA, thiourea, KSCN etc.), and finally sonicated in order to produce stable sols of DNDs, which will be achieved via final surface adjustments as suggested in *Fig. 9 (iii).* An alternative removal of the unwanted sp^2 carbon phases based on formation and selective decomposition of intercalates and acetylides, and high-frequency melting of metallic impurities will be also tested. Finally, secondary detonation treatments with the aim to control level of defects and multishell structure of DND will be tested.

The complete characterization will be carried out by synergy of various direct (SEM, HR TEM) and indirect (XRD) structural probes to inspect regularity and internal structural arrangement within a single particle, vibrational (FTIR, Raman sp.) and electron spectroscopies (XPS, UV/VIS), elemental composition analysis (EDAX, ICP MS, XRF), surface properties (BET, surface charge), and DLS. The extended characterization of the physical properties by means of luminescence, volume and local magnetometries including magneto-luminescence/Raman spectroscopy studies and EPR, will be carried out to verify the functional response of the final DND product prefunctionalized for further linking.

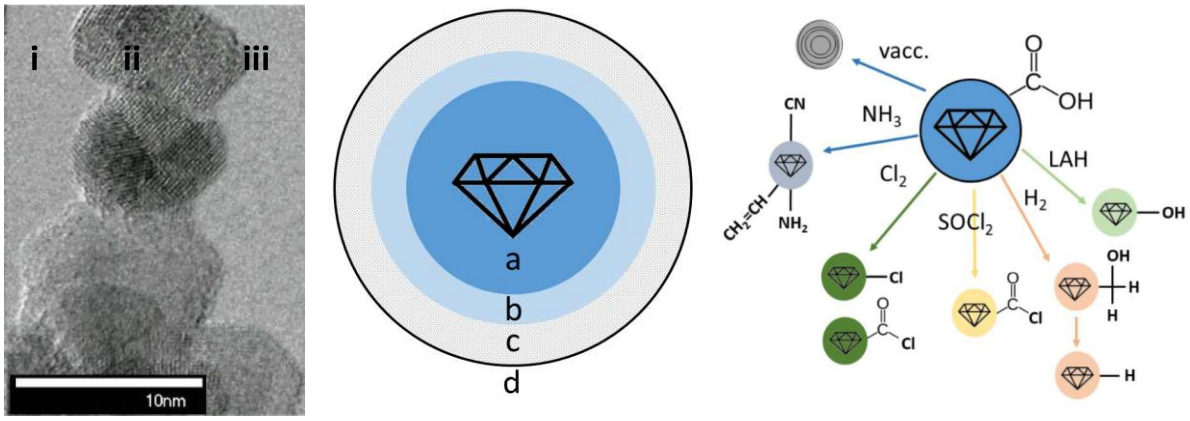

Fig. 9: Characteristic appearance of a DND particle and its surface modification. (i) Typical TEM image of DND particles revealing aglomeration, crystalline diamond facets and defected shells (adopted from reference [5]). (ii) Schematic representation of the internal structure of a DND particle (ii): a – sp^3 crystalline diamond core, b – defected diamond layer, c – carbonaceous (sp^2) shell, d – surface layer with carboxyle group termination; the typical size of the DND particle is 5 nm. (iii) Scheme of possible modification strategies starting form carboxyl - functionalized purified DND.

WP2:	**Nanodiamonds**
Objectives	
• To establish route(s) for preparation of nanodiamonds by detonation synthesis with high yield. • To establish purification protocols for preparation of high-purity detonation nanodiamond (DND). • To develop robust and coupling-favorable surface modification(s) of DND for nanolinking and interfacing. • To test alternatives for *ab initio* control of defect-based species and other intrinsic properties of DND.	
Activities	
A2.1.: Preparation of DND **Duration: M1 – M48**	

Duration	**Task description**	**Involved groups**
M1-M16	Optimization of detonation and explosion batches by variation of chemical composition, ratio of components, final processing, and geometry.	OZM
M1-M18	Verification of composition and morphology of a rationalized series of detonation batches by suitable methods (SEM, XRD, FTIR) yielding formulation of the first generation of detonation batches.	MFF UK, UFCH, FZU, UOCHB
M12-M24	Preparation of DND in the experimental chamber using first generation detonation batches.	OZM

M12-M28	Step by step analysis of the diamond soot (DS) obtained by the first generation of detonation batches with respect to sequencing of the detonation (after each detonation cycle vs. after complete detonation cycle): definition of the most significant impurities and their aggregation state (XRD, ICP MS, XPS, XRF, SEM, EDX), quantification of the sp^3 to sp^2 content (XPS, Raman spectroscopy), determination of the particle size and crystallinity of the sp^3 component (XRD, SAXS, HR TEM).	MFF UK, UFCH, FZU, UOCHB
M18-M36	Preparation of DND in the experimental chamber using second generation detonation batches (optimized according to the high yield and DND quality based on the results from the first generation experiments).	OZM
M18-M40	Step by step analysis of the diamond soot (DS) obtained by the second generation of detonation batches in the same vein as for the first generation of DND.	MFF UK, UFCH, FZU, UOCHB
M32-M48	Preparation of DND in the experimental chamber using detonation batches with alternative composition (metal-free, metal-enriched).	OZM
M32-M48	Step by step analysis of the DS obtained by the alternative detonation batches in the same vein as for the first and second generations of the DND.	MFF UK, UFCH, FZU, UOCHB
Milestone MS2.1 in M18: Targeted composition of the detonation batch for high yield preparation of DND.		
Milestone MS2.2 in M40: Reproducible methodology for preparation of DND using conventional detonation batches.		
Deliverable D2.1 in M40: Summary report on the optimized procedure of DND preparation.		
Deliverable D2.2 in M48: Summary report on the procedures of DND modification using alternative detonation batches.		
A2.2.: Purification of DND **Duration: M1 – M48**		
Duration	**Task description**	**Involved groups**
M1-M12	Purification of testing DND - purchased from commercial suppliers - in gas phase (thermooxidative treatment, Cl_2, H_2, H_2O), and evaluation of the most effective route(s).	UFCH, MFF UK
M1-M12	Purification of testing DND in liquid phase (acidic and oxidative acidic treatment, use of strong complexing agents), evaluation of the most effective route(s).	MFF UK, UFCH, UOCHB
M1-M16	Sequential analysis of the raw and purified testing DND: definition of the most significant impurities and their aggregation state (XRD, ICP MS, XPS, XRF, SEM, EDX), quantification of the sp^3 to sp^2 content (XPS, Raman	MFF UK, UFCH, FZU, UOCHB

	spectroscopy), determination of the particle size and crystallinity of the sp^3 component (XRD, SAXS, HR TEM).	
M12-M24	Step 1 - Purification of first generation DS: macroseparation and acidic treatment	OZM, UFCH
M12-M28	Sequential analysis of the first generation DS using the protocol optimized for the as-obtained DS (defined in A2.1) and the testing DND samples.	MFF UK, UFCH, FZU, UOCHB
M16 – M30	Step 2a - Purification of first generation DND in laboratory scale: gas phase treatments of the DS subjected to step 1.	UFCH, MFF UK
M16 – M30	Step 2b - Purification of first generation DND: liquid phase treatments of the DS subjected to step 1 in laboratory scale.	UFCH, MFF UK, UOCHB
M20 – M36	Step 3 - Purification of first generation DND: high-temperature treatment in vacuum of the first generation DND treated by Steps 2 in laboratory scale.	MFF UK, UFCH
M16 – M36	Sequential analysis of the DND (first and second generation) purified by the step 2a,b and 3 using the protocol optimized for the testing DND.	MFF UK, UFCH, FZU, UOCHB
M20 – M40	Step 1 - second generation DS in laboratory scale.	OZM, UFCH
M20 – M40	Step 2a,b - second generation DND in laboratory scale.	UFCH, MFF UK, UOCHB
M26 – M42	Step 3 - second generation DND in laboratory scale.	MFF UK, UFCH
M24 – M42	Modification of purification steps 1 – 3 for the DS and DND obtained by using alternative detonation batches.	OZM, MFF UK, UFCH
M32 – M48	Sequential analysis of the DS obtained by using alternative detonation batches after purification step 1.	MFF UK, UFCH, FZU, UOCHB
M32 – M48	Sequential analysis of the DND obtained by using alternative detonation batches after purification steps 2a, 2b and 3.	MFF UK, UFCH, FZU, UOCHB
Milestone MS2.3 in M28: Optimized methodology for effective extraction, separation and basic purification of DND.		
Milestone MS2.4 in M42: Optimized methodology for fine purification of DND.		
Deliverable D2.3 in M28: Summary report on optimization of extraction, separation and basic purification of DND.		
Deliverable D2.4 in M42: Summary report on optimization of fine purification of DND.		
A2.3. Intrinsic and surface modifications of DND **Duration: M13 – M48**		
Duration	**Task description**	**Involved groups**
M1-M12	Surface chemical modification of testing DND based on controlled surface activation by thermal annealing *in vacuo* followed by modification using linkers bearing	UOCHB, UFCH

	diazonium salts proceeded under bead assisted sonic disintegration (BASD) conditions.	
M1-M12	Complex analysis (structure, morphology, surface charge, particle size) of the modified testing samples of DND using established characterization techniques and protocols: FTIR, Raman spectroscopy, XRD, SAXS, SEM, HR TEM, DLS, MALS, BET.	UOCHB, MFF, UFCH, FZU
M12-M36	Surface chemical modification of the first and second generation DND with maximized purity based on controlled surface activation by thermal annealing *in vacuo* followed by modification using optimized linkers bearing diazonium salts proceeded under BASD conditions.	UOCHB, UFCH
M12-M40	Complex analysis (structure, morphology, surface charge, particle size) of the modified first and second generation of DND samples with maximized purity using established characterization techniques and protocols: FTIR, Raman spectroscopy, XRD, SAXS, SEM, HR TEM, DLS, MALS, BET.	UOCHB, MFF UK, UFCH, FZU
M30-M48	Secondary detonation treatment of the purified DND.	OZM
M30-M48	Preparation of DND using light element enriched detonation batches.	MFF UK, UFCH, UOCHB, FZU
M30-M48	Sequential analysis of the DND obtained by using secondary detonation treatment and alternative detonation batches.	MFF UK, UFCH, UOCHB, FZU
Milestone MS2.5 in M36: Convenient chemical route(s) for surface modification of purified DND with precursors for nanolinking.		
Milestone MS2.6 in M48: Conclusions on impact of secondary detonation treatment and enrichment with light elements.		
Deliverable D2.5 in M40: Summary report on strategies for surface functionalization of purified DND with precursors of nanolinks.		
Deliverable D2.6 in M48: Summary report on strategies for intrinsic modifications of DND.		

Milestones

Nr.	Month	Description
MS2.1	18	Targeted composition of the detonation batch for high yield preparation of DND.
MS2.2	40	Reproducible methodology for preparation of DND using conventional detonation batch.
MS2.3	28	Optimized methodology for effective extraction, separation and basic purification of DND.
MS2.4	42	Optimized methodology for fine purification of DND.

MS2.5	36	Convenient chemical route(s) for surface modification of purified DND with precursors for nanolinking.
MS6	48	Conclusions on impact of secondary detonation treatment and enrichment with light elements.
Deliverables		
Nr.	Month	**Description**
D2.1	40	Summary report on the optimized procedure of DND preparation.
D2.2	48	Summary report on the procedures of DND modification using alternative detonation batches.
D2.3	28	Summary report on optimization of extraction, separation and basic purification of DND.
D2.4	42	Summary report on optimization of fine purification of DND.
D2.5	40	Summary report on strategies for surface functionalization of purified DND with precursors of nanolinks.
D2.6	48	Summary report on strategies for intrinsic modifications of DND.

WP2 GANTT Chart																	
	2018	2019				2020				2021				2022			
A2.1.: Preparation of DND																	
Optimization of detonation and explosion batches.																	
Verification of composition and morphology of a rationalized series of detonation batches.																	
Preparation of DND in the experimental chamber using first generation detonation batches.																	
Step by step analysis of the diamond soot (DS).																	
Preparation of DND in the experimental chamber using second generation detonation batches.																	
Step by step analysis of the DS obtained by the second generation of detonation batches.																	
Preparation of DND in the experimental chamber using detonation batches with alternative composition.																	
Step by step analysis of the DS obtained by the alternative detonation batches.																	
A2.2.: Purification of DND																	
Purification of testing DND - purchased from commercial suppliers - in gas phase.																	
Purification of testing DND in liquid phase.																	
Sequential analysis of the raw and purified testing DND.																	
Step 1 - Purification of first generation DS: macroseparation and acidic treatment.																	
Sequential analysis of the first generation DS and the testing DND samples.																	
Step 2a - Purification of first generation DND in laboratory scale: gas phase treatments of the DS subjected to step 1.																	
Step 2b - Purification of first generation DND: liquid phase treatments of the DS subjected to step 1 in laboratory scale.																	
Step 3 - Purification of first generation DND: high-temperature treatment in vacuum of the first generation DND treated by Steps 2 in laboratory scale.																	
Sequential analysis of the DND (first and second generation).																	
Step 1 of second generation DS in laboratory scale.																	
Step 2a,b second generation DND in laboratory scale.																	
Step 3 second generation DND in laboratory scale.																	
Modification of purification steps 1 – 3 for the DS and DND obtained by using alternative detonation batches.																	
Sequential analysis of the DS obtained by using alternative detonation batches after purification step 1.																	

WP2 GANTT Chart																		
	2018	2019				2020				2021				2022				
Sequential analysis of the DND obtained by using alternative detonation batches after purification steps 2a,b, 3.																		
A2.3. Intrinsic and surface modifications of DND																		
Surface chemical modification of testing DND based on controlled surface activation.																		
Complex analysis of the modified testing samples of DND.																		
Surface chemical modification of the first and second generation DND with maximized purity based on controlled surface activation.																		
Complex analysis of the modified DND samples of the first and second generation.																		
Secondary detonation treatment of the purified DND.																		
Preparation of DND using light element enriched detonation batches.																		
Sequential analysis of the DND obtained by using secondary detonation treatment and alternative detonation batches.																		