WP1: Graphenoids

Research strategy and methodology

The main goal of the WP1 is the preparation of ultra-pure and defined graphenoids (graphene, carbon nanotubes – CNTs), their chemical functionalization with covalent links, their structurization and lithographical modifications

The Activity 1.1 deals with optimization of the substrates for native and funcionalized graphene. Our preliminary results show that graphene – copper single crystal interaction depends on the surface face. This motivates further study on copper foil where grains of different orientation can by identified by EBSD. After the transfer process the same place will be identified and the quality of the graphene will be evaluated by number of methods (Raman spectroscopy, SEM, AFM). The realization of the activity 1.1 will enable to discover relation between copper – graphene interaction and the success of the transfer process. The activity 1.1 is directly connected to WP3, WP4 and WP5.

The Activity 1.2. aims at preparation of ultra-pure graphenoids (graphene, CNT) and their covalent chemical functionalization. The purification methods applied on CNT will be based on our previous experiences and will be optimized for specific samples used in the project. We have previously demonstrated that graphene can be modified by different type of reactions (radical, nucleophilic and electrophilic substitutions), which provides large set of options for specific desired modification of graphenoids. As for the linkages, for example reversible amine-aldehyde condensation or alkyne-azide Huisgens dipolar cycloaddition are proposed for covalently dynamic or rigid cross-linking, respectively.

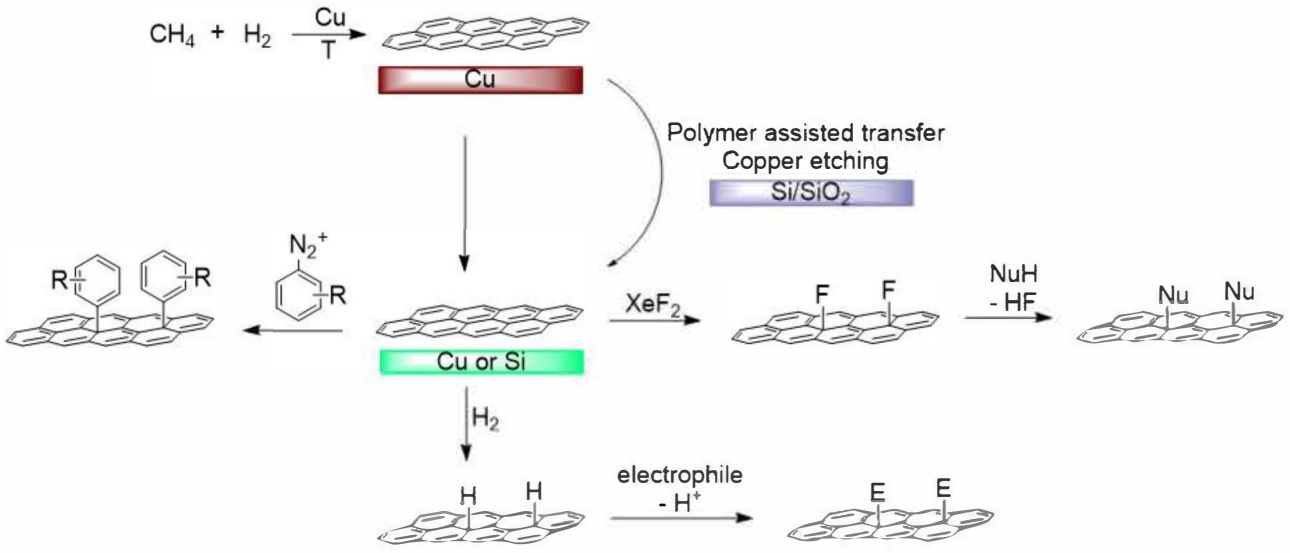

Fig. 8: Types of chemical reactions to introduce the corresponding functional groups

Introduction of the corresponding functional groups will be achieved via several types of reactions (see **Chyba! Nenalezen zdroj odkazů.**) which offers broad range of chemical compatibility between the introduced chemical moieties and the functionalization conditions. Functionalized graphenoids will be further used in WP3 and WP4 to study interactions with diamond particles and to prepare hybrid materials. Furthermore, in WP4 and WP5 the functional layers will be tested for sensing properties.

The Activity 1.3 deals with lithographic structuring of graphenoids and substrates for their growth. The lithography is very useful method to provide fine topographic structures. In case of copper substrate, the lithography will enable to create specific periodic shapes on a microscale. The modification of the topography will be made before growth of the graphene; thus the graphene growth on periodic structures can be tested. In addition, the lithography will be combined with anisotropic chemical etching reactions.

For application in microelectrodes or microsensors graphene needs to be patterned. The lithography is the obvious option as it is well established and scalable. In case of graphene there are some challenges which include, avoiding the graphene damage and /or modification during the lift off or etching process. Different resists and etching procedures will be tested to find optimum conditions for production of unperturbed patterned structures. The prepared samples will be further used in WP3 for preparing patterned hybrid structures and in WP4 and WP5 for fabrication of sensors and homo-composites.

<table>
<tr><th colspan="2">WP1:</th><th>Graphenoids</th></tr>
<tr><td colspan="3">Objectives</td></tr>
<tr><td colspan="3">• Topographic and structural optimization of substrates for native and functionalized graphene for tunable adhesion.
• Optimization of purification and chemical functionalization of graphenoid carbons for effective mutual linkage.
• Optimization of lithographic procedures for fine structuring of graphene and substrates.</td></tr>
<tr><td colspan="3">Activities</td></tr>
<tr><td colspan="3">A1.1.: Topographic a structural optimization of substrates
Duration: M1 – M48</td></tr>
<tr><td>Duration</td><td>Task description</td><td>Groups involved</td></tr>
<tr><td>M1-M18</td><td>Growth of graphene by Low pressure CVD on copper foil and copper single crystals.</td><td>UFCH, TESLA</td></tr>
<tr><td>M12-M36</td><td>Topographic modification of the copper substrate using DND. Characterisation of the modified substrates using AFM, XPS. Growth of graphene on topographically modified copper substrate.</td><td>UFCH, FZU, TESLA, MFF UK</td></tr>
<tr><td>M6-M42</td><td>Identification of the surface phase orientation of copper substrate under CVD grown graphene using EBSD,</td><td>UFCH, FZU, TESLA</td></tr>
</table>

	determination of the interaction using Raman spectroscopy, AR PES.	
M9-M36	Transfer of graphene and determination of the surface face orientation on the transferred graphene. Measurement of SEM, EBSD, Raman spectroscopy, AFM.	UFCH, FZU, TESLA, MFF UK
M18-M48	Transfer of graphene and determination of the surface topography modification on transferred graphene. Measurement of SEM, EBSD, Raman spectroscopy, AFM.	UFCH, FZU, TESLA, MFF UK
Milestone MS1.1 in M36: Identified optimum surface orientation of the copper substrate for graphene transfer.		UFCH, FZU, TESLA, MFF UK
Milestone MS1.1 in M48: Identified optimum surface topography of the copper substrate for graphene transfer.		UFCH, FZU, TESLA, MFF UK
Deliverable D1.1 in M38: Summary report on the dependence of transfer process on surface orientation of the copper substrate.		UFCH, FZU, TESLA, MFF UK
Deliverable D1.2 in M48: Summary report on the dependence of transfer process on surface topography of the copper substrate.		UFCH, FZU, TESLA, MFF UK
A1.2.: Chemical functionalization and purification of graphenoid carbons Duration: M1 – M48		
Duration	**Task description**	**Groups involved**
M1-M9	Design, formulation and synthesis of linker molecules with the ability to be covalently linked to sp^2 carbon networks.	UFCH, UOCHB
M2-M18	Purification and testing of CNT purchased from commercial suppliers - in gas phase (thermooxidative treatment, hot steam treatment, alkyl metal treatment, vacuum high temperature annealing) and evaluation of the most effective route(s).	UFCH, TESLA
M4-M24	Analysis of the purified testing CNT, identification of the important impurities and monitoring of the effect of purification on diameter distribution, defect creation and electronic properties of CNT (Raman spectroscopy, TG, UV-ViS spectroscopy, ICP MS, XPS, SEM, EDX) and magnetic characterisation.	UFCH, MFF UK, UOCHB
M2-M18	Activation of graphenoid carbons by simple molecules-oxidation, fluorination and hydrogenation. Characterization of the functionalized graphenoids by surface sensitive methods (Raman spectroscopy, AFM, XPS, TPD, SEIRA, MS).	UFCH, UOCHB, MFF UK
M12-M36	Functionalization of pristine/ pre functionalized CNT with linker molecules such as amines, aldehydes, alkynes and azides for covalently dynamic cross-linking or Huisgens dipolar cycloaddition.	UFCH, UCHB

M12-M42	Functionalization of pristine/ prefunctionalized graphene on specific substrates (topographically modified copper) with linker molecules such as amines, aldehydes, alkynes and azides for covalently dynamic cross-linking or Huisgens dipolar cycloaddition.	UFCH, UCHB
MM16-M42	Characterization and analysis of the functionalized CNT by Raman spectroscopy, TG, UV-ViS spectroscopy, ICP MS, XPS, SEM, EDX. Electrical measurements and microscopic measurements (AFM, HR TEM).	UFCH, UCHB, ZCU
M16-M48	Characterization and analysis of the linker molecules functionalized graphene by Raman spectroscopy, AFM, XPS, TPD, SEIRA, MS, optical spectroscopy incl. ellipsometry, contact angle), electrical measurements of conductivity	UFCH, UCHB, MFF UK, ZCU
Milestone MS1.3 in M24: Optimized methodology for effective purification of CNT.		UFCH, MFF UK, UOCHB, TESLA
Milestone MS1.4 in M42: Optimized methodology for functionalization of graphenoid carbons.		UFCH, UCHB, MFF UK, ZCU
Deliverable D1.3 in M24: Summary report on optimization of methodology for efficient purification of CNT.		UFCH, MFF, UOCHB, TESLA
Deliverable D1.4 in M42: Summary report on optimization of methodology for functionalization of graphenoid carbons.		UFCH, UCHB, MFF UK, ZCU
A1.3. Lithographic structuring of graphenoids and substrates **Duration: M13 – M48**		
Duration	**Task description**	**Groups involved**
M1-M12	Design of basic structures and corresponding photolithographic masks.	UFCH, FZU, ZCU
M3-M36	Preparation of electrodes from graphene on Si/SiO_2 substrate.	UFCH, FZU, TESLA
M6-M24	Lithographic topography modification of the copper substrate.	UFCH, FZU,Tesla
M6-M48	Characterisation of the topography of lithographically modified graphene AFM, SEM, electrical measurements.	UFCH, FZU, MFF UK, ZCU
M9-M30	Characterisation of the topography of lithographically modified substrates by AFM, SEM, XRD.	UFCH, FZU, MFF UK
M18-M46	Optimization of the lithography protocol for obtaining graphene microelectrodes.	UFCH, FZU, TESLA
Milestone MS1.5 in M24: Methodology for lithographical modification of copper substrate nanotopography.		UFCH, FZU, ZCU
Milestone MS1.6 in M46: Optimized methodology for lithographical modification of graphene.		UFCH, FZU, MFF UK, ZCU
Deliverable D1.5 in M36: Summary report on methodology for lithographical modification of copper substrate nanotopography.		UFCH, FZU, ZCU

Deliverable D1.6 in M48: Summary report on methodology for lithographical preparation of graphene microelectrodes on Si/SiO_2 substrate.	UFCH, FZU, MFF UK, ZCU

Milestones

No.	Month	Description
MS1.1	M36	Identified optimum surface orientation of the copper substrate for graphene transfer.
MS1.2	M48	Identified optimum surface topography of the copper substrate for graphene transfer.
MS1.3	M24	Optimized methodology for effective purification of CNT.
MS1.4	M42	Optimized methodology for functionalization of graphenoid carbons.
MS1.5	M24	Methodology for lithographical modification of copper substrate nanotopography.
MS1.6	M46	Optimized methodology for lithographical modification of graphene.

Deliverables

No.	Month	Description
D1.1	M38	Summary report on the dependence of transfer process on surface orientation of the copper substrate.
D1.2	M48	Summary report on the dependence of transfer process on surface topography of the copper substrate.
D1.3	M24	Summary report on optimization of methodology for efficient purification of CNT.
D1.4	M42	Summary report on optimization of methodology for functionalization of graphenoid carbons.
D1.5	M36	Summary report on methodology for lithographical modification of copper substrate nanotopography.
D1.6	M48	Summary report on methodology for lithographical preparation of graphene microelectrodes on Si/SiO_2 substrate.

WP1 GANTT Chart																	
	2018	2019				2020				2021				2022			
A1.1.: Topographic and structural optimization of substrates																	
Growth of graphene by Low pressure CVD.																	
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A1.3. Lithographic structuring of graphenoids and substrates																	
Design of basic structures and corresponding photolithographic masks.																	
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