SEVENTH FRAMEWORK PROGRAMME
THE PEOPLE PROGRAMME

International Research Staff Exchange Scheme

Annex I - "Description of Work"

Version dated 6/02/2014
Amendment n°1: Termination of a beneficiary, Addition of one or more beneficiaries, Modification of Annex I

PART A

1. Grant agreement details

Full Title: Tuning the properties of NanoCarbon with Fluorination

Acronym: NanoCF

Proposal Number: 612577

Scientific Panel: Chemistry

Grant Agreement Number: PIRSES-GA-2013-612577

Duration of the project: 48 months

2. List of participants (*beneficiaries* and partner organisations)

Participant Number	Participant name	Participant short name	Country
1 *Beneficiary* 1 (coordinator)	Leibniz-Institut für Polymerforschung Dresden e.V.	IPF DRESDEN	DE
2 *Beneficiary* 2	University of Vienna	UNIVIE	AT
3 *Beneficiary* 3	CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE	CNRS	FR
4 *Beneficiary* 4	FRIEDRICH-ALEXANDER-UNIVERSITAT ERLANGEN NURNBERG	FAU	DE
5 *Beneficiary* 5	University of Mons	UMONS	BE
6 Partner 6	Changchun Institute of Applied Chemistry	CIAC	CN
7 Partner 7	Nikolaev Institute of Inorganic Chemistry, Siberian Branch of RAS, Novosibirsk	NIIC SB RAS	RU
8 Partner 8	M.M. Semiakin - Yu.A. Ovchinnikov Institute of bioorganic	IBCH RAS	RU
9 Partner 9	Nagoya University	NU	JP
10 Partner 10	Zhejiang University	ZJU	CN
11 Partner 11	THE UNIVERSITY OF SYDNEY	USYD	AU

3. Project summary

Low-dimensional carbon structures such as graphene and carbon nanotubes have raised tremendous interest in recent years both from fundamental and technological perspectives. However, the tunability of the density of electronic states of graphene and carbon nanotubes remains a limiting factor for their implementation in modern nanotechnology. It has been recently shown that the energy bandgap of graphene-based materials can be tailored via chemical modification of the graphene surface, e.g. by fluorination. We focus our efforts on tuning the chemical and physical properties of nanocarbon materials using different fluorination techniques and varying the degree of fluorination. A multidisciplinary approach will be applied ranging from fundamental research in chemistry and physics to studying the materials properties for application in electronics, photonics, and biomedicine. It is anticipated that the final outcome of this project will be a novel nanocarbonbased material with specific advanced properties.

PART B

4. Quality of the Exchange Programme

4.1 Objectives and relevance of the joint exchange programme

The network NanoCF is designed to exploit the potential of fluorinated nanocarbon materials for application in electronics, photonics, or biomedicine. A multidisciplinary approach will be applied ranging from fundamental research in chemistry and physics to studying the materials properties for technological innovation. To be specific, within the present project we want to:

- Synthesize carbon-based materials of different allotropic forms and morphology (carbon nanotubes with various numbers of walls, graphene and few-layered graphene);
- Modify them by fluorination using different approaches (room- and high-temperature synthesis, plasma) and varying the fluorine concentration;
- Investigate the effects of chemical modification in order to find a relationship between the processing routes and structure of fluorocarbon materials;
- Study the chemical and physical properties of the fluorinated carbon to compare different starting materials and fluorination approaches with a focus on tailoring their materials properties;
- Evaluate their use as elements of nanoelectronics and optoelectronics (*transistors, conducting wires, lasers, etc.)*, luminescent markers (*nanoparticles-based diagnostics*), active sensing layers (*gas sensor technology*) and electrode coating (*efficient battery materials*).

Low-dimensional carbon structures such as graphene and carbon nanotubes have raised tremendous interest in recent years both from fundamental and technological perspectives. However, the tunability of the density of electronic states of graphene and carbon nanotubes remains, until now, a limiting factor for their implementation in modern nanotechnology. Recent discoveries enable tailoring of the energy bandgap of graphene-based materials via chemical modification of the graphene surface, e.g. by fluorination. We focus our efforts on tuning the chemical and physical properties of nanocarbon materials using different fluorination techniques and varying the degree of fluorination. It is anticipated that the final outcome of this project will be a novel nanocarbon-based material with specific advanced properties.

The strength of this proposal is the implementation of a complete “synthesis-characterisation-device implementation” loop for fluorinated nanocarbon materials. A specific example of such a loop within the proposed network is that the synthesis of carbon materials is performed in the CNRS (Toulouse), followed by fluorination in the NIIC SB RAS and radical induced plasma functionalization in the USYD, the characterisation part at the IBCH RAS (electron and scanning microscopy), IPF DRESDEN (NMR-spectroscopy), CNRS (optical spectroscopy), UMONS (photoelectron spectroscopy) and UV (optical transitions) assisted by the theoretical part, which is implemented in UN, CIAC and CNRS (quantitative interpretation of the spectra and modelling of fluorination patterns), and, finally, proof-of-concept devices are tested in ZJU (nanocomposites), NIIC SB RAS (gas sensing), CNRS (cathode materials) and FAU (field-effect- and magnetoresistance measurements). All components of the proposed feedback loop are ready to be executed. The synergies between the partners will serve as building blocks for the proposed project and the exploitation of pre-existing connections, which ensure a quick start-up of the project, will reinforce the partnership and provide a good consortium for achieving the project objectives.

The scientific and management objectives of the project are organized in 4 Work Packages (WP). The WP will be guided by project leaders from the partner institutions.

4.2. Work Packages

Table 1: List of Work Packages

WP n°	Work Package Title	Beneficiary/Partners	Start month	End month
1	Management	IPF DRESDEN	1	48
2	Synthesis and Functionalisation	CNRS, NIIC SB RAS, USYD, UMONS	1	42
3	Characterisation and theoretical modelling	IBCH RAS, IPF DRESDEN, NU, CIAC, CNRS	3	48
4	Property investigation and tuning	UMONS, UNIVIE, ZJU, FAU, NIIC SB RAS, CNRS	5	48

This section is further categorized by the WP. In general, each WP except for the WP 1 Management comprises several research Tasks that focus upon the local capacities available from the partners. The exchange program is planned to meet the experimental demands of each Task, which require either performing supplementary investigations, which are not-available at the home laboratory, or brainstorming joint activity for the interpretation of the obtained results. During the visits of experienced researchers (ER), details of the study will be refined and results of the investigations will be discussed. The early stage researchers (ESR) will do the experimental and computational work using the resources available at the partner's laboratories.

Table 2: Work Packages[1]

Work Package n°	1	**Start date or starting event:**	Month 1
Work Package Title	Management		
***Beneficiary*/Partner Organisation**	IPF DRESDEN		
Objectives: 1) to maintain direct contacts with the Commission and to perform the general management of the project and the communication within the consortium by: checking the progress of the work, establishing an yearly report for the EC Commission and taking control of the formal modification or closing of different work packages, collecting the scientific and financial reports; 2) to organize meetings aimed at exchanging information and optimizing the cooperation among the partners, to organize Annual Meetings with the EC Commission to review the progress of the project, to organize an Internal Intermediate Evaluation Meeting; 3) to nominate a Advisory Board.			
Description of work Task 1.1: Coordination The IPF Dresden will be the coordinator of the project. It will be in charge of the supervision of the project progress and coordination of the initiative and it will be also the main interface between the partners and the European Commission. It is responsible for reporting, delegation of work packages, motivation of the team, encouragement of creativity, correct problem solving procedures and corrective actions. The project coordinator will be particularly responsible for co-ordinating the contract negotiation, arrangement of meetings regarding time, logistics, documentation and follow-up actions, notification to partners of reporting requirements and follow up, collection of scientific information and collation into reports, distribution of all scientific reports to the Commission and partners and preparation and submission of financial reports. Formal reports will be sent to the EC to meet the circular pattern expected by the Commission together with financial statements. To ensure that the project results are accurate and reported correctly			

[1] The researchers identified by this Annex I can be replaced by other researchers in accordance with the definitions contained in Art. III.1.

(quality management), the Co-ordinator will ask all the partners to keep detailed records of input and output within the project using logbooks/ timecard system and to ensure the scientific rules according to good laboratory praxis (GLP).

Task 1.2: Meetings

The Coordinator will devote particular attention to ensure communication within the consortium members and with all committees. A specific "Kick-off" meeting will be scheduled at the beginning of the project in order to ensure a quick project start. Periodically meetings will be organized to exchange information and requirements of the project progress. The Annual Meetings with the EC Commission shall review the progress of the project. After 24 months the coordinator has to arrange a meeting for an internal evaluation of the project with all partners and the EC officer. Agendas for all meetings will be required. Discussions, decisions and actions will be recorded. The structure for monitoring and reporting progress will consist of a series of reports and meetings. Progress of each task will be assessed continuously to ensure that there is no - or limited- deviation from the original plan and to closely control the development activities of the partners. The minutes meeting will be required to identifying variance against objectives/giving details of corrective action/ achievements.

Task 1.3: Committees

The Advisory Board will be established latest in month 3. The board will be comprised of highly experienced professionals from academic science and industry in the fields of bionanotechnology and energy nanotechnology. The network will establish an *Advisory Board*, which will monitor and evaluate the progress of the research program and advice future strategies within and possibly beyond the contract period.

Deliverables

D1.1 Organisation of the Kick-off meeting (Month 1)
D1.2: Creation of Advisory Board (Month 3)
D1.3: Organisation of the Internal Intermediate Evaluation Meeting (Month 24)
D1.4: Management Report (Months 12, 24, 36, 48)
D1.5: Collecting of the deliverables and financial reports (continuously)
D1.6: Preparation of the "Periodic reports" and "Final Report" (Months 12, 24, 36, 48)

Researchers involved: Anastasia Vyalikh (researcher), Sandra Martinka (EU-Referentin)

Staff secondments and transfer of knowledge

MNG: from P1 to P8, involved in Task 1.2 (M1.2) for deliverables D1.4. and D1.6

Risk management

A lack of productivity or quality, delays and other disagreements can be typical contentious issues during a project. The coordinator will have the obligation of identifying these conflicts as early as possible and taking actions to resolve the problem. Negotiations and decisions made by consensus will be important actions for solving the conflicts. In the case that a decision is not achievable with majority, the coordinator will involve the EC Project Officer or another expert outside the project.

Work Package n°	2	**Start date or starting event:**	Month 1
Work Package Title	Synthesis and Functionalisation		
***Beneficiary*/Partner Organisation**	CNRS, NIIC SB RAS, USYD, UMONS		

Objectives

Carbon-based low-dimensional materials will be synthesized and further functionalized by adding fluorine atoms using different methods. State-of-the-art microscopy and spectroscopy methods will be used to characterise the pristine carbon materials. Further, functionalisation with fluorine atoms will be performed in a controllable way to modify the properties of the resulting materials. In order to achieve controlled levels of fluorination, different routes, such as room- and high-temperature methods as well as plasma-based fluorination will be addressed in Tasks 2.3 and 2.4. Finally, fluorinated nanocarbons will be used for development of hybrids from nanocarbons and

semiconducting nanoparticles (quantum dots).

Description of work

Task 2.1: Synthesis of carbon nanotubes (CNRS, key person: Emmanuel Flahaut)

Different kinds of Carbon Nanotubes (CNTs) will be prepared adjusting the catalyst composition and/or the Catalytic Chemical Vapour Desposition (CCVD) parameters (including a carbon source, which is usually CH_4, EtOH or C_2H_4). Adding a nitrogen-containing molecule, for example, acetonitrile, in the carbon feedstock will be used to develop the synthesis of nitrogen-doped double-walled CNTs, which are expected to have different reactivity toward fluorinating agents as compared to pure CNTs. For preparation of few-walled CNTs, which could have some advantage compared to the double-walled CNTs as electrode material for energy storage, we will investigate cluster bimetallic molecules like keplerates as a catalyst source. Our preliminary experiments have shown that the latter has a perspective for the CCVD synthesis of few-walled CNTs (mostly 3-5 walls). Within the present project we will optimize the synthesis parameters to obtain nanotubes with narrow diameter distribution.

Chemical purification of CNTs (by oxidation in solution or in air and by heating in inert atmosphere or in high vacuum) will also be performed prior to functionalisation as it is important to functionalize only CNTs and not other carbon by-products which are usually also present in raw samples.

Task 2.2: Synthesis of graphene (NIIC SB RAS, key person: Alexander Okotrub)

To prepare graphene and few-layered graphene we will use intercalation compounds of graphite fluoride C_2F with different guest molecules. The semifluorinated graphite $(C_2F)_n$ is synthesized by an original method developed at the NIIC SB RAS, where a gaseous BrF_3, which acts as a fluorinating agent, is diluted with Br_2 to optimize the fluorination process. Synthesis carried out at room temperature (usually takes 1 month) yields graphite fluoride intercalated with Br_2 molecules. The guest molecules will be replaced by desirable organic molecules (acetonitrile, heptane, dichloromethane, etc.) through a set of exchange reactions in solution in order to give first-stage intercalates with interlayer distances ranging from 0.6 to 1.5 nm depending on the intercalant molecule.

To prepare graphene layers from graphite fluoride C_2F the following approaches will be adopted: (1) Few-layered graphene will be obtained by thermal exfoliation of C_2F. Our preliminary results show that thermal shock of C_2F intercalated with Br_2 at 800ºC yields graphene stacks consisting of 5 layers in an average with a lateral size of hundred microns. The effect of intercalant and temperature on a number of layers in a stack will be studied. Particular attention will be paid to prevent functionalisation of graphene layers by oxygen-containing groups by exfoliating graphite fluoride under inert atmosphere. (2) A method of exfoliation of graphite fluoride in a solution based on ultrasonication will be developed. Therefore appropriate organic solutions and surface active compounds will be adjusted, and the sonication parameters, such as power and duration, will be optimized. To isolate graphene layers, we will try spin-coating, aerobashing, or tension techniques. (3) Finally, the conducting graphene-like layers will be produced directly on the surface of C_2F with accurate removal of fluorine atoms as a result of sample surface irradiation by high-energy particles (electrons or Ar+ ions) or by the treatment with hydrazine vapors. Our preliminary experiments show that this approach is very promising for obtaining of p-doped conducting graphene layers on the top of the insulating C_2F substrate. Such hybrid structure can be directly implemented into gas sensing or nanoelectronic devices.

Task 2.3: Room- and high-temperature fluorination (NIIC SB RAS, key person: Lyuba Bulusheva)

Since the curved surface of a CNT is more reactive than the flat graphene surface, it can be fluorinated to the C_2F composition using F_2 at temperatures lower than required to produce semifluorinated graphite (250ºC vs. 350ºC) or at room temperature using volatile inorganic fluorides such as BrF_3 or ClF_3. However, it is difficult to increase the fluorine loading higher than 50% because the inner side of a nanotube wall is usually inaccessible for a fluorinating agent. Within the Task 2.3 we will specifically open the nanotube ends using an oxidative procedure with the subsequent sample annealing in an inert atmosphere to check the reactivity of the inner nanotube surface. The CNT samples obtained within the Task 2.1 will be fluorinated by F_2 gas at an elevated temperature or by BrF_3 at room temperature. We will vary the synthesis temperature from 100 to 250ºC as well as the ratio of Br_2:BrF_3 to change the concentration of the fluorinating agent.

Fluorination of graphite will be performed at room temperature by the method described in the

Task 2.2. Especial efforts will be made towards decreasing the concentration of fluorine atoms attached to the graphene layers. Tuning the ratio of Br_2:BrF_3 and varying the duration of synthesis we expect obtaining the graphite fluoride CF_x with x from 0.1 to 0.5. Since we expect that the few-layered graphene favores fluorination compared to bulk graphite, we will develop a method for fluorination of few-layered graphene produced within the Task 2.2. Mechanical exfoliation or sonication in a solution will be applied to obtain fluorinated graphene.

Task 2.4: Plasma fluorination (UMONS, key person:Carla Bittencourt)

Among the reported fluorination methods plasma-based functionalisation methods have the advantage to be solvent-free, time efficient and flexible as it provides a wide range of functional groups depending on the plasma parameters. In addition, conversely to fluorination via wet-chemistry, fluorination via cold plasmas has the potential to limit fluorination to the surface of the nanostructure thus reducing degradation effects. While for non-aligned carbon nanotubes strategies for surface functionalisation without impacting their properties are established, strategies for optimal functionalisation of vertical aligned CNTs and graphene flakes are lacking. Based on our preliminary studies fluorination will be performed by exposing aligned CNTs and few-layer graphene to fluorine chemical species generated in a RF or □-wave cold plasmas or by gas thermal cracking (CF_4 and F_2 (diluted in Ar)). Treatments with CF_4 plasma can lead to thin film deposition; however during our preliminary tests we established parameters that prevent film deposition. Because the energy distribution and the nature of the species generated in these functionalisation methods are different (i.e. presence of ions in the plasma), we expect to observe differences in the nature of the grafted functional group and/or the fluorine addition pattern. A major challenge will be the determination of optimal reproducible functionalisation parameters allowing the grafting of selected functional groups. In this context, a deep understanding of the plasma-surface interaction will be necessary. Therefore, state-of-the-art energy-resolved mass spectroscopy will be used to evaluate the chemical composition and energetic of the plasma.

Task 2.5: Radical induced plasma functionalization (USYD, key person: Marcela Bilek)

Recent studies have shown that highly active radicals can be embedded in fluorinated carbon materials by plasma processes ranging from high-energy low-pressure pulsed plasmas to atmospheric plasmas. We will develop a range of plasma processes to create reactive radicals for functionalization. Their utility will be demonstrated by functionalization with bioactive molecules. The activity of the radicals and the results of functionalization will be investigated using methods that include FTIR-ATR, XPS, and ESR spectroscopies

Task 2.6: Preparation of hybrids (CNRS, key person: Emmanuel Flahaut)

The fluorinated CNTs and graphene will be used for attaching of the semiconducting nanoparticles, such as CdS, Cu_2S, ZnS, etc for the graphitic surface. As semiconducting nanomaterials can emit and/or absorb light and possess fascinating optical properties, hybridizing such nanocrystals with CNTs or graphene is expected to modify their optical characteristics and luminescent properties significantly. Within the Task 2.6 we will focus on the grafting of fluorescein molecule (isothiocyanate derivative, FITC), which is appropriate as a fluorescent marker. Being attached to the surface of a double-walled CNT (e.g., for drug delivery purpose), this marker can be used to track the position of the nanotubes. This is also extremely useful for toxicity studies of such nanoparticles. Again, the grafting of organic molecules to create the hybrids will be performed after fluorination of the samples and will be compared to direct grafting after oxidation. It is known that conducting graphitic surface is quenching photoluminescence. One strategy to limit the quenching is to increase the distance between the graphitic surface and the luminescent probe. Here we will examine the photoluminescence efficiency of the hybrids attaching the semiconducting nanoparticles or FITC molecules through a linker. Diamines of different lengths will be used for this purpose. The linking of amine molecules to the graphitic surface will be carried out using a nucleophilic substitution of fluorine atoms. Thus fluorination of CNTs and graphene will be used for the creation of reactive sites for nucleation for direct growth of nanoparticles, as well as for the helping in further functionalisation with amines.

Deliverables

D2.1: A set of the samples enriched with the double-walled and few-walled carbon nanotubes purified from the by-products (Month 8)

D2.2: Samples of carbon nanotubes and graphene flakes with different fluorinated groups grafted at the surface (Month 12).

D2.3: Samples of graphene films and few-layered graphene films on different kinds of insulating

substrates such as silicon dioxide, quartz, graphite fluoride C_2F. Free-standing thin films of graphene obtained through a filtration procedure (Month 24).
D2.4: Samples of nanostructured C_xF_y films (e.g., fluorinated nano/mesoproous carbon, CNTs, and graphene) on a variety of substrates (ITO, Si, metals, glass, etc.) (Month 24).
D2.5: Samples of fluorinated carbon nanotubes, graphite fluoride, and fluorinated graphene with different fluorine concentration (Month 36).
D2.6: The hybrid samples of CNTs with attached fluorescein molecules and semiconducting nanoparticles; the graphene decorated with semiconducting nanoparticles (Month 42).

Researchers involved (the researchers are numbered as ERx.y, where x is the number of beneficiary, y is the number of a researcher for each beneficiary)
Task 2.1: ER: Emmanuel Flahaut (ER3.1); ESR: Elena Shlyakhova (ESR3.1), Dmitry Gorodetskii (ESR3.2)
Task 2.2: ER: Alexander Okotrub (ER7.1), Igor Asanov (ER7.2); ESR: Yulia Fedoseeva (ESR7.1), Vyacheslav Tur (ESR7.2)
Task 2.3: ER: Lyuba Bulusheva (ER7.3), ESR: Alexander Nazimov (ESR7.3), Victor Koroteev (ESR7.4)
Task 2.4: ER: Carla Bittencourt (ER5.1), Rony Snyders (ER5.2), Dany Cornelissen (ER5.3); ESR: Mattia Scardamaglia (ESR5.1), Claudia Struzzi (ESR5.2)
Task 2.5: ER: Marcela Bilek (ER11.1), David McKenzie (ER11.2), Alexey Kondyurin (ER11.3)
Task 2.6: ER: Emmanuel Flahaut (ER3.1), Anne Marie Galibert (ER3.2), Brigitte Soula (ER3.3); ESR: Tifania Bortolamiol (ESR3.3)

Staff secondments and transfer of knowledge
ER3.1: from P3 to P7, involved in Task 2.1 (M2.1) for deliverables D2.1
ERS3.1: from P7 to P3, involved in Task 2.1 (M2.1) for deliverables D2.1
ERS3.2: from P7 to P3, involved in Task 2.1 (M2.1) for deliverables D2.1
ER7.1: from P7 to P1, involved in Task 2.2 (M2.3) for deliverables D2.3
ER7.2: from P7 to P1, involved in Task 2.2 (M2.3) for deliverables D2.4
ERS7.1: from P7 to P1, involved in Task 2.2 (M2.3) for deliverables D2.4
ERS7.2: from P7 to P1, involved in Task 2.2 (M2.3) for deliverables D2.3
ER7.3: from P7 to P3, involved in Task 2.3 (M2.4) for deliverables D2.2
ERS7.3: from P7 to P3, involved in Task 2.3 (M2.4) for deliverables D2.3
ERS7.4: from P7 to P5, involved in Task 2.3 (M2.4) for deliverables D2.3
ER5.1: from P5 to P7, involved in Task 2.4 (M2.2) for deliverables D2.2 and D2.5
ERS5.1: from P5 to P7, involved in Task 2.4 (M2.2) for deliverables D2.2 and D2.5
ER5.2: from P5 to P11 involved in Task 2.4 and 2.5 (M2.2) for deliverables D2.2 and D2.5
ERS5.2: from P5 to P11 involved in Task 2.4 and 2.5 (M2.2) for deliverables D2.2 and D2.5
ER5.3: from P5 to P11, involved in Task 2.4 and 2.5 (M2.2) for deliverables D2.5
ER3.2: from P3 to P7, involved in Task 2.6 (M2.5) for deliverables D2.6
ER3.3: from P3 to P7, involved in Task 2.6 (M2.5) for deliverables D2.6
ESR3.3 from P3 to P7, involved in Task 2.6 (M2.5) for deliverables D2.6

Risk management
Tasks 2.2 and 2.3: Although the methods of fluorination of nanocarbon have been well established, the pre-defined chemical composition could be difficult to achieve. The problem will be overcome by applying 4 different fluorination approaches.
Tasks 2.4: Fluorine plasmas can be very aggressive destroying the carbon nanostructures, however functionalization outside the glow region can reduce the damages.
Tasks 2.4 and 2.5: 2 or 3 different processing methods utilizing a range of ion energies and plasma pressures for fluorinated carbon materials will be employed to ensure the creation of radicals effective for functionalization.

Work Package n°	3	**Start date or starting event:**	Month 3
Work Package Title	Characterisation and theoretical modelling		
***Beneficiary*/Partner Organisation**	IBCH RAS, IPF DRESDEN, NU, CIAC, CNRS		

Objectives

Preliminary experimental results and first-principles calculations show that the material we are dealing with represents a remarkably complex physical system characterised by the presence of spatially correlated disorder. Thus, complete understanding of the structure of fluorinated carbon materials and their physical properties can be achieved only by using a combination of experimental and theoretical methods. Structural modification due to fluorination and the evolution of the electronic properties of the functionalized carbon-based nanostructures will be studied by combining microscopy techniques (TEM, SEM and AFM) with spectroscopic methods (XPS, UPS, NEXAFS and NMR). Theoretical modelling of chemisorption processes as well as first-principle calculations of the electronic and molecular structure and dynamics, vibrational and optical spectra and NMR parameters will be applied for interpretation of the experimental trends, and prediction of routes to optimize synthesis routes for optimal materials properties.

Description of work

Task 3.1: Microscopy and vibrational spectroscopy (IBCH RAS, key person: Ekaterina Obraztsova)

Vibrational spectroscopies are known to be very informative for carbon materials characterisation. Raman measurements using Jobin Yvon U 1000 and Jobin Yvon S 300 instruments with excitation at a wide range of wavelengths in visible region will be applied to the materials prepared within Tasks 2.2-2.4. IR absorption measurements will be realized using Bruker Vertex 70v instrument operating in middle and far infrared region. The materials synthetized in WP 2 will be characterised using these techniques in order to reveal diamond-to-graphene transformations under thermal treatment in vacuum. Additionally, selective graphite etching during thermal oxidation will be in situ monitored. We expect that obtained results will allow development of models describing formation and modification of carbon film materials.

Monitoring the topology peculiarities and atomic structure is critically important for high yield synthesis and efficient modification of the nanocarbon materials. The structural characterisation using three complimentary microscopic techniques: atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) will be performed in order to study the correlation of the materials optical and electronic properties, synthesis and subsequent modification parameters.

Task 3.2: Fluorine patterning (NMR and DFT) (IPF DRESDEN, key person: Anastasia Vyalikh)

A combination of solid-state nuclear magnetic resonance (NMR) spectroscopy and density functional theory (DFT) calculations of NMR parameters will be used to elucidate the structure of graphite fluorides produced in Task 2.2. The distribution of the fluorine atoms over the graphitic layer and fluorine patterns formation is determined based on distinct ^{19}F solid state NMR signals, whose assignment is supported by the first-principle calculations. Recently it has been established that all possible fluorination motives may co-exist in low-temperature graphite fluorides disproving the presence of uniform structural motives, such as e.g. chains. Thus, a previously developed classification catalogue for assignment of ^{19}F NMR chemical shifts based on DFT calculations will be used to identify and quantify the structural motives obtained upon fluorination. Heteronuclear correlation NMR experiments, which enable to probe interactions between the graphitic matrix and intercalated molecules selectively, or between the graphitic matrix and functionalized groups, will be employed to characterise the host – guest interactions in fluorinated graphite intercalation compounds and to edit the spectra on the base of through-space dipolar interactions. The results will be compared with the microscopy data provided in Task 3.1 and with the simulation data of final fluorination patterns on the graphitic surfaces calculated in Task 3.4. Further, this approach will be applied to fluorinated CNT to investigate fluorination patterns in these materials.

Task 3.3: Fluorine chemisorption (DFT) (NU, key person: Stephan Irle)

Carbon nanomaterial - fluorine interaction potentials will be calculated with high accuracy using *ab initio* and density functional theory (DFT) methods. As nanomaterials, carbon nanotubes as well as graphene, pristine and doped where applicable will be employed. The highly accurate potentials will be applied to develop parameters for the computationally very efficient density-functional tight-binding (DFTB) method previously elaborated and successfully tested for the case

of graphene hydrogenation. The new DFTB parameters will allow MD simulations and the simulation of vibrational spectra as described in Task 3.4.

Task 3.4: Simulations of fluorine sputtering (MD) and vibrational spectra (CIAC, key person: Ying Wang)

Nonequilibrium MD simulations based on a quantum chemical potential (QM/MD) on chemical sputtering of atomic fluorine beams on graphene and other nanocarbon materials will be performed using new parameters of C-F developed in Task 3.3 for the computationally very efficient density-functional tight-binding (DFTB) method. A single-layer graphene model system consisting of a large planar unit cell including vacuum layer, and an algorithm for atomic F additions will be employed will be employed. A sufficiently large number of trajectories will be computed with varying conditions, such as environmental temperature as well as projectile kinetic energies. The results will be analyzed in terms of evolving fluorination patterns on the graphitic surfaces, as well as in terms of associated reaction energy profiles and computed vibrational spectra compared with the experimental results provided in Tasks 3.1-3.2.

Task 3.5: Characterising fluorinated nanocarbons by simulation (CNRS, key person: Chris Ewels)

This computational task can be divided into two parts: (i) identifying the atomic structure of graphite fluoride; adatom diffusion and self-organization pathways leading to it; the dependence of structure on the controllable external parameters (temperature, stoichiometry, etc.); and (ii) investigating the electronic structure and magnetic properties of the materials as well as the corresponding structure-property relations.

First-principles computational techniques based on the DFT formalism is the most widely used atomistic tool for investigating the structure and physical properties of materials. This task will focus on investigating structural motifs present in fluorinated graphene CF_x at various stoichiometries ($0 < x < 1$). The chemical mechanisms of fluorination will also be investigated. This will incorporate the effect of different carbon structures (mono- and multi-layers) and determine the role of solvent layers. We will also investigate structural dynamics, such as migration barriers and defect structure coupling, in order to understand and predict surface rearrangement behaviour allowing preferential stabilisation of ferromagnetic structural motifs. Wherever possible we will calculate properties such as vibrational absorption frequencies and simulate electron micrographs for direct comparison with experimental data obtained in Tasks 3.1. First-principles calculations based on DFT will be performed using the publicly available AIMPRO code based on the Gaussian-type atomic orbital basis sets.

Deliverables

D3.1: AFM and TEM images of fluorinated nanocarbon. (Month 24)

D3.2: A report describing the results of optical spectroscopy studies of fluorinated nanocarbons samples (Month 32).

D3.3: NMR study of fluorinated CNT and graphite fluoride at different degree of fluorination (Month 36).

D3.4: High-level *ab initio,* first principles, and preliminary DFTB potential energy reaction pathways for the attack of *one* or two fluorine atom on pyrene and coronene model systems for the graphite (0001) surface (Month 36).

D3.5: Improved DFTB parameters for chemical reactions of fluorine atoms on graphite surfaces, including vacancy and other defects (Month 40).

D3.6: A report on the study of correlation between the morphology and optical properties of nanocarbons at different stages of synthesis and fluorination (Month 48).

D3.7: High-level *ab initio,* first principles, and DFTB potential energy surfaces for fluorine atoms intercalated between graphite layers (Month 48).

Researchers involved

Task 3.1: ER: E.A. Obraztsova (ER8.1), D.V. Klinov (ER8.2), A.I. Chernov (ER8.3),; ESR: F.T. Tuyakova (ESR8.1), A.V. Belkin (ESR8.2), A.A. Tonkikh (ESR8.3)

Task 3.2: ER: Anastasia Vyalikh (ER1.1), Ulrich Scheler (ER1.2), De-Yi Wang (ER1.3)

Task 3.3: ER: Stephan Irle (ER10.1)

Task 3.4: ER: Ying Wang(ER6.1), Zhijian Wu(ER6.2); ESR: Menggai Jiao (ESR6.1)

Task 3.5: ER: Chris Ewels (ER3.4); ESR: Jean-Jo Adjizian (ESR3.4), Philipp Wagner (ESR3.5), Olga Sedelnikova (ESR3.6)

Staff secondments and transfer of knowledge
ER8.1: from P8 to P2, involved in Task 3.1 (M3.1) for deliverables D3.1, D3.6
ER8.1: from P8 to P3, involved in Task 3.1 (M3.1) for deliverables D3.1,D3.2, D3.6
ER8.2: from P8 to P4, involved in Task 3.1 (M3.1) for deliverables D3.2
ESR8.1: from P8 to P3, involved in Task 3.1 (M3.1) for deliverables D3.1,D3.2
ESR8.2: from P8 to P4, involved in Task 3.1 (M3.1) for deliverables D3.1, D3.2
ESR8.3: from P8 to P4, involved in Task 3.1 (M3.1) for deliverables D3.1, D3.2
ER1.1: from P1 to P6, involved in Task 3.2 (M3.4) for deliverables D3.3.
ER1.1: from P1 to P7, involved in Task 2.2, 2.3 and 3.2 (M3.1) for deliverables D3.3
ER1.1: from P1 to P8, involved in Task 3.1 and 3.2 for deliverables D3.3
ER1.3: from P1 to P9, involved in 4.3 for deliverables D4.4
ER1.2: from P1 to P10, involved in Task 3.2 and 3.3 for deliverables D3.3
ER1.2: from P1 to P11, involved in Task 2.5 and 3.3 for deliverables D3.3
ER10.1: from P10 to P2, involved in Tasks 3.3 and 4.2 (M3.2, M3.3) for deliverables D3.4, D3.5 and D4.3
ER6.1: from P6 to P4, involved in Task 3.4 (M3.4. M3.5) for deliverables D3.5 and D3.7
ESR6.1: from P6 to P4, involved in Task 3.4 (M3.4. M3.5) for deliverables D3.5 and D3.7
ER3.4: from P3 to P8 and P7, involved in Task 3.5 (M3.4) for deliverables D3.6
ERS3.4: from P3 to P8, involved in Task 3.5 (M3.4) for deliverables D3.6
ERS3.5: from P3 to P7, involved in Task 3.5 (M3.4) for deliverables D3.6.
ERS3.6: from P7 to P3, involved in Task 3.5 (M3.4) for deliverables D3.6

Risk management
Although the characterisation methods are well established and routinely applied to the differently modified CNTs and graphene-like structures, the use of these techniques for fluorine-doped carbon nanomaterials is challenging and might be inefficient.
Then for Task 3.1 specific approaches will be applied such as substrate selection, substrate surface modification, alteration of the deposition method (for AFM, SEM, TEM methods) and use of different surfactants for suspension preparation, selection of excitation energies and spectral regions (for optical measurements).
For Task 3.2 a sensitivity issue can be a problem in NMR spectroscopy, particularly in the samples with a very low degree of fluorination and of low quantity. An isotope-labelling approach can be used for the sample preparation to increase sensitivity of ^{13}C NMR.
In general, different experimental techniques will be applied for characterisation of each sample, which provide the complementary information.

Work Package n°	4	**Start date or starting event:**	Month 5
Work Package Title	Investigating and tuning the properties		
***Beneficiary*/Partner Organisation**	UMONS, UNIVIE, FAU, ZJU, NIIC SB RAS, CNRS		

Objectives
Electronic and optical properties as well as transport, reactivity and thermal conductivity will be studied with a focus on the impact of surface-functionalisation and variation of synthesis conditions on the materials properties and device performance. This WP aims on tailoring materials properties and their further optimisation towards applications in electronics, photonics, and biomedicine.

Description of work
Task 4.1: Experimental electronic structure (size of π-system, band gap) (UMONS, key person:Carla Bittencourt)
The chemical modifications due to the grafting will be evaluated by x-ray photoelectron spectroscopy and contact angle measurements, possible impact in the morphology and structure will be evaluated by TEM and SEM. The dispersion of metal clusters that weakly interact with the surface of G-LDSs (such as gold) will be used to monitor the presence and distribution of active sites such as morphological and/or chemical defects. Thermal evaporated atoms will be used,

after the deposition the dispersion of the metal atoms will be observed by TEM. Combined with microscopy (TEM, SEM, and AFM), XPS, UPS and NEXAFS will be used to evaluate structural modification due to functionalisation and to study the evolution of the electronic properties of the functionalized materials. This combination will contribute towards a better understanding of defect formation and fundamental mechanisms of the chemical modification.

Task 4.2: Optical properties (optical gap, luminescence) (UNIVIE, key person: Alexander Grüneis)

Optical transitions in the fluorinated graphene, graphite, and double-walled CNTs will be studied in comparison with those in the initial carbon materials. The spectra between 0.5 and 6.4eV will be measured with a Hitachi U3410 spectrometer. A BRUKER 66V spectrometer with attached IR-Raman spectrometer is used in order to determine vibronic properties and the electronic response in the infrared region. Since the optical response is governed by the joint density of states, it shows a characteristic behavior. For example, for graphene, it depends on the number of layers. Functionalisation with fluorine would induce gaps in the described materials and this will be observable using optical spectroscopy. With a Dilor Raman spectrometer using an ArKr and a tunable TiSa laser we will perform polarization dependent measurements to investigate the anisotropic optical properties. This is particularly interesting for aligned nano ribbons, which have an interesting and complex Raman spectrum that has never been analyzed in detail.

Task 4.3: Flame retardancy, electric and thermal conductivity (ZJU, key person: Hong Fan)

Fluorinated nanocarbon will be used to prepare a series epoxy-based nanocomposite (0.1 wt%, 0.2 wt% and 0.5 wt% loading of fluorinated nanocarbon). The flame retardant properties, electric properties and thermal conductivity of these polymer nanocomposites will be investigated. In comparison, the conventional nanocarbon will be used to prepare corresponding polymer nanocomposites. This study will help to evaluate whether the fluorinated nanocarbons have the potential of being used in such high performance polymer nanocomposites field.

Task 4.4: Electronic transport properties (FAU, key person: Vojislav Krstić)

Electrical measurements on devices with integrated fluorinated nanomaterials will be performed, focusing on the impact of surface-functionalisation and variation of synthesis conditions on the device performance. Feedback to simulation and modelling as well as device-integration tasks will be analyzed to ensure targeted material- and device-performance improvements. We will focus on contribution to electrical contacting protocols and technology for the project's nanomaterials adjusted specifically to the type of fluorinated material. Predominant measurement techniques applied will be field-effect measurements and magnetoresistance measurements at varying temperature using both DC and AC (phase-sensitive detection) as well as photoconductivity measurements.

Task 4.5: Gas sensing (NIIC SB RAS, key person: Alexander Okotrub)

Gas sensing properties will be examined for the fluorinated graphitic samples produced within the Tasks 2.2 and 2.4. As it has been previously demonstrated the partially defluorinated layers located on the insulator fluorinated graphite substrate are very effective for the sensing of ammonia. The quick response is provided by electric conductivity of the restored graphene layers, while the high sensitivity to gas molecules is due to p-doping of graphene still preserving a small amount of CF groups. In the current project we will study the sensing properties of graphitic materials depending on the number of restored surface layers and concentration of the rest fluorine. Sensitivity of sensors towards NO_2, CH_4, NH_3, Cl_2, EtOH gases will be checked.

Task 4.6: Ionic transport (CNRS, key person: Patrice Simon)

The synthesized fluorinated carbon materials (few-layered graphene, carbon nanotubes) will be tested as cathodes in Li-batteries. Samples will be processed into films using the conventional PVDF-binder technique and coin cells will be assembled (materials to be tested as the cathode in front of a Li anode) and tested in 1M LiPF6 EC-DEC electrolyte. The specific capacity and powder and energy density will be determined. The obtained values will be correlated with the structural parameters (specific surface, number of layers, defects), fluorine content, and electric conductivity of the samples.

Deliverables

D4.1: Electrical contacting and charge-injection into one or more types of fluorinated nanomaterials (Month 18).

D4.2: Electrical field-effect characterisation of one or more types of fluorinated nanomaterials (Month 24).

D4.3: Interpretation of resonance Raman spectra of fluorinated carbon nanomaterials (Month 36).

D4.4: Determination of the impact of the different fluorination strategies in the electronic structure of the graphene-based low-dimensional nanostructures (Month 42).
D4.5: Flame Retardant properties, electric properties and thermal conductivity of fluorinated nanocarbon based epoxy nanocomposites report. (Month 42).
D4.6: Temperature-dependent transport measurements of one or more types of fluorinated nanomaterials (Month 44).
D4.7: Magnetic-field dependent transport measurements of a few types of fluorinated nanomaterials (Month 47).
D4.8: Determination of sensitivity and selectivity of the recovered fluorinated carbon layers in interactions with molecules (Month 47).
D4.9: Lithium ion transport in the fluorinated carbon nanomaterials (Month 48).

Researchers involved
Task 4.1: ER: Carla Bittencourt (ER5.1), Rony Snyders (ER5.2), Dany Cornelissen (ER5.3); ESR: Mattia Scardamaglia (ESR5.1), Claudia Struzzi (ESR5.2)
Task 4.2: ER: Alexander Grüneis (ER2.1); ESR: Nikolay Verbitskiy (ESR2.1)
Task 4.3: ER: Hong Fan, (ER9.1), Cheng Li (ER9.2), ESR: Zhen Jin (ESR9.3)
Task 4.4: ER: Vojislav Krstić (ER4.1), Maria Kolesnik (ER4.2); ESR: Stephen Connaughton (ESR4.1), Eleanor Holmes (ESR4.2)
Task 4.5: ER: Alexander Okotrub (ER7.1), Mikhail Katkov (ER7.4); ESR: Mikhail Kanygin (ESR7.4)
Task 4.6: ER: Patrice Simon (ER3.5), E. Flahaut (ER3.1); ESR: P.L. Taberna (ESR3.7), Ekaterina Fedorovskaya (ESR3.8)

Staff secondments and transfer of knowledge
ER5.1: from P5 to P7 involved in Task 4.1 (M4,1 and M4.6) for deliverables D4.2, 4.4 and D4.5
ESR5.1: from P5 to P7 involved in Task 4.1 (M4,1 and M4.6) for deliverables D4.2 and D4.5
ESR5.2: from P5 to P7 involved in Task 4.1 (M4,1 and M4.6) for deliverables D4.2 and D4.5
ESR2.1 from P2 to P6 involved in Tasks 3.4, 4.2 (M4.2) for D4.5
ER2.1 from P2 to P7 involved in Task 4.5 (M4.2) for D4.8
ESR2.1 from P2 to P7 involved in Task 4.5 (M4.2) for D4.8
ESR2.1 from P2 to P8 involved in Task 3.1 (M4.2) for D3.1
ER2.1 from P2 to P10 involved in Tasks 3.1 and 4.2 (M4.2) for D4.4 and D4.5
ESR2.1 from P2 to P10 involved in Task 3.1 and 4.2 (M4.2) for D4.4 and D4.5
ER9.1: from P9 to P1, involved in Task 4.3 (M4.2) for deliverables D4.5
ER9.2: from P9 to P1, involved in Tasks 3.2 and 4.3 (M4.7) for deliverables D3.3 and D4.5
ERS9.3: from P9 to P1, involved in Task 4.3 (M4.7) for deliverables D4.5
ER4.1: from P4 to P7 and P8, involved in Task 4.4 (M4.3 and M4.6) for deliverables D4.1, D4.2, D4.6, D4.7
ER4.2: from P4 to P8, involved in Task 4.4 (M4.3) for deliverables D4.1and D4.7
ERS4.1: from P4 to P7, involved in Task 4.4 (M4.3) for deliverables D4.1 and D4.2
ERS4.2: from P4 to P7, involved in Task 4.4 (M4.3) for deliverables D4.6 and D4.7
ER7.1: from P7 to P2, involved in Task 4.5 (M4.4) for deliverables D4.8
ER7.4: from P7 to P4, involved in Task 4.5 (M4.4) for deliverables D4.8
ERS7.4: from P7 to P5, involved in Task 4.5 (M4.4) for deliverables D4.8
ER3.5: from P3 to P8 and P7, involved in Task 4.6 (M4.5 and M4.6) for deliverables D4.9.
ER3.1: from P3 to P8, involved in Task 4.5 (M4.5) for deliverables D4.9.
ERS3.7: from P3 to P7, involved in Task 4.6 (M4.5) for deliverables D4.9.
ERS3.8: from P7 to P3, involved in Task 4.6 (M4.5) for deliverables D4.9.

Risk management
Sensibility of certain techniques may not be enough to probe certain changes in properties due to the fluorination at low concentration. Partners have experience in complementary techniques that can give indirect information.
Task 4.1 Availability of certain techniques are bound to the accepted beamline proposals. Partners having beamtime accepted for projects not directly related to NanoCF will perform

measurements in at least two shifts of beamtime.
Task 4.4 Unstable contact-interfaces due to increased chemical reactivity between fluorinated nano-carbons and metal electrodes may become an issue which would require the need for developing a technological process for post-device integration fluorination using suitable capping and shielding layers such as low-reactive resists PMMA or MAN.
Task 4.3 Nano-dispersivity of fluorinated graphite in epoxy composites may become an issue. Therefore 2 or 3 different processing methods for fluorinated nanocarbon based epoxy nanocomposites will be employed.
Tasks 4.3-4.6 Properties to be investigated are based on the results reported in literature and on scientific foresights of the partners. We anticipate that at least 3 of 5 application aspects tested within the WP4 will be successfully realized.

Table 3: List of Milestones

List and schedule of milestones			
Milestone n°	**Milestone name**	**Lead *Beneficiary* organisation short name**	**Delivery date**
M1.1	Organisation of the kick-off meeting	IPF DRESDEN	2-3
M1.2	Organisation of network workshops	IPF DRESDEN	12,24,36
M2.1	Development of the methods for producing CNTs with a controlled number of walls. Elaboration of procedures for purification of CNTs	CNRS	12
M2.2	Determination of the plasma parameters to control the grafting of selected fluorinated groups to obtain the C_4F and C_2F pattern	UMONS	20
M2.3	Development of the methods for preparing large-size graphene and few-layered graphene from graphite fluoride. Development of the methods for preparing conducting graphene-like layers with a controlled thickness on the surface of insulating C_2F support	NIIC SB RAS	24
M2.4	Elaboration of the methods for controlling the stoichiometry of the outer walls of CNT, fluorinated graphene, and graphite fluoride through the room-temperature or high-temperature fluorination	NIIC SB RAS	36
M2.5	Development of the methods for uniform attaching of semiconducting nanoparticles and fluorescein molecules to the surface of fluorinated CNTs and graphene	CNRS	42
M3.1	Revealing the structure and functionality of fluorocarbon	IBCH RAS	36
M3.2	DFTB parameters for fluorine-graphite interactions	NU	24
M3.3	Improved DFTB parameters for fluorine interactions intercalated between graphite layers	NU	40
M3.4	Elucidation of structural motifs present in fluorinated graphene at different stoichiometries	CIAC	48
M3.5	Increasing the number of F atoms stepwise to investigate the fluorination structure evolution with time and to further achieve controlled fluorination by changing environmental conditions	CNRS	48
M4.1	Electronic structure determination by using X-ray spectroscopy	UMONS	42

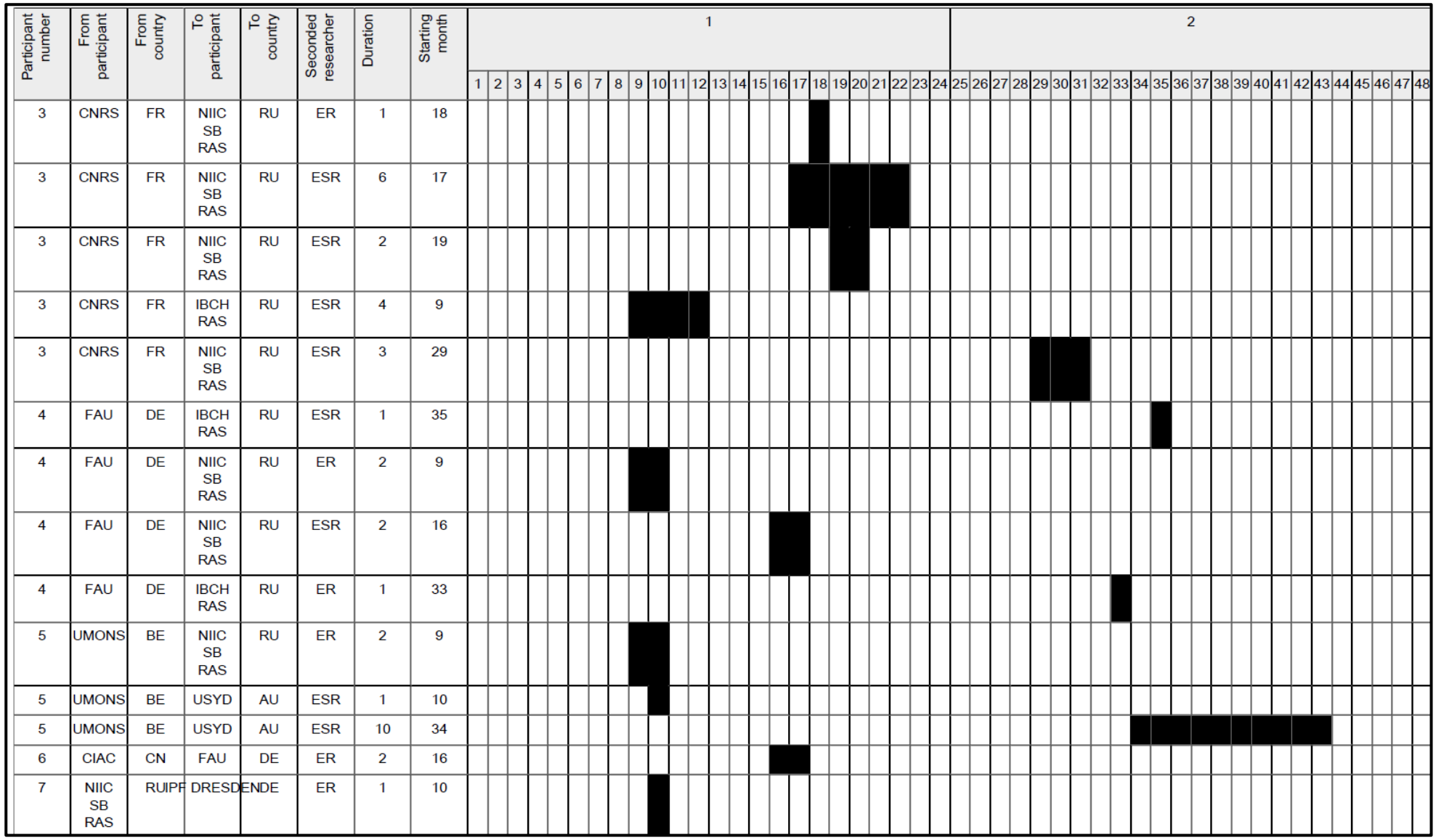
M4.2	Determination of optical gap in carbon-based materials depending on the fluorination degree	UNIVIE	42
M4.3	Charge transport in the fluorinated and recovered carbon structures	FAU	47
M4.4	Reactivity and sensing of the recovered fluorinated nanocarbon surface towards gas molecules with different chemical nature	NIIC SB RAS	47
M4.5	Efficiency of fluorocarbon materials in the primary lithium-ion battery	CNRS	48
M4.6	Evaluation of the aging effects in fluorocarbon materials	UMONS	48
M4.7	Preparation of fluorinated nanocarbon based epoxy nanocomposites with nano-dispersion	ZJU	40

Table 4: Gantt chart of secondments[2]

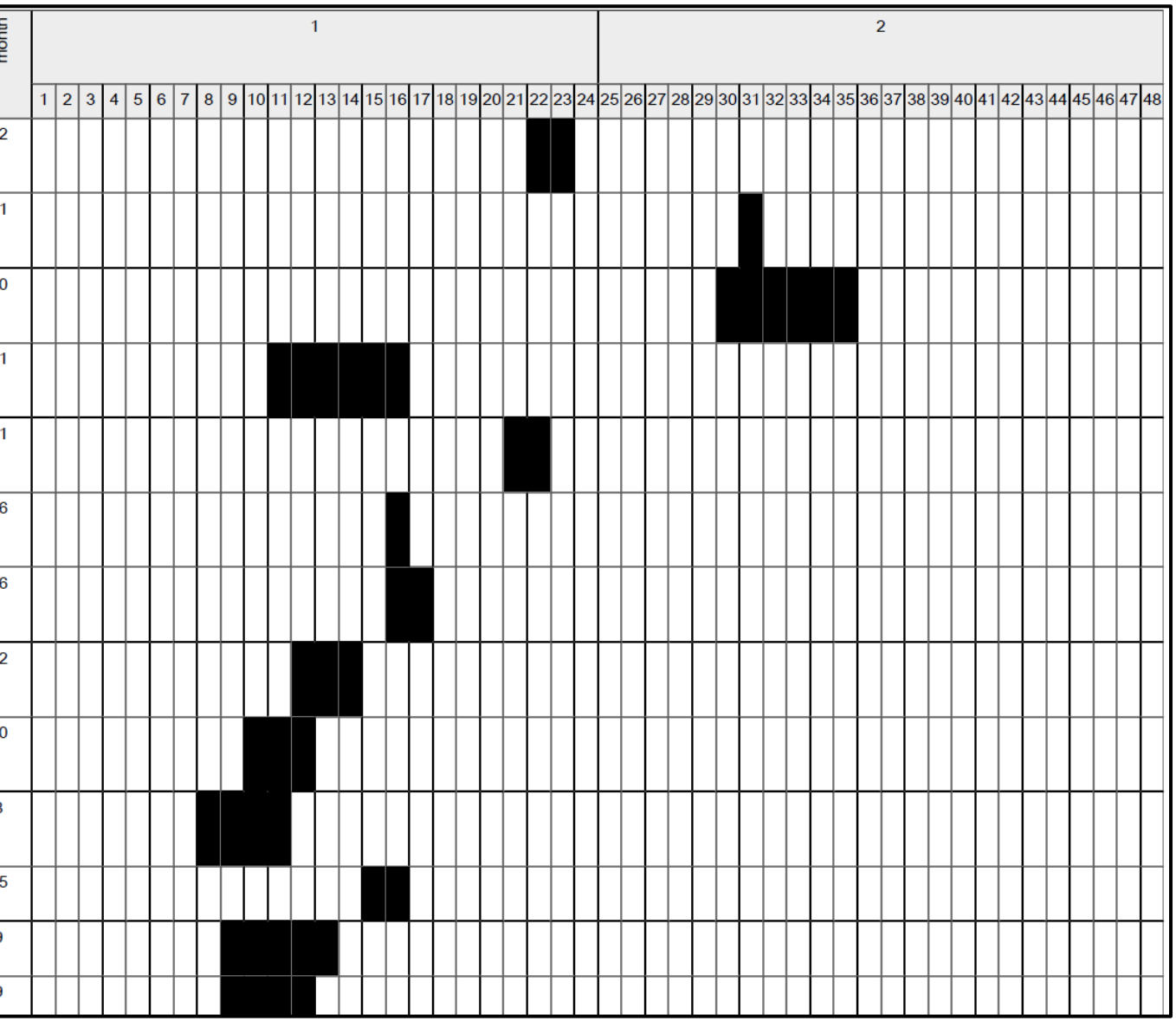
Participant number	From participant	From country	To participant	To country	Seconded researcher	Duration	Starting month
1	IPF DRESDEN	DE	CIAC	CN	ESR	1	23
1	IPF DRESDEN	DE	NIIC SB RAS	RU	ER	1	34
1	IPF DRESDEN	DE	IBCH RAS	RU	ER	1	12
1	IPF DRESDEN	DE	IBCH RAS	RU	MS	1	36
1	IPF DRESDEN	DE	NU	JP	ER	1	25
1	IPF DRESDEN	DE	ZJU	CN	ER	1	32
1	IPF DRESDEN	DE	USYD	AU	ER	1	42
2	UNIVIE	AT	IBCH RAS	RU	ESR	2	10
2	UNIVIE	AT	NIIC SB RAS	RU	ER	1	22
2	UNIVIE	AT	NU	JP	ESR	2	9
2	UNIVIE	AT	NU	JP	ER	4	9
2	UNIVIE	AT	CIAC	CN	ER	1	8
2	UNIVIE	AT	NIIC SB RAS	RU	ESR	2	22
3	CNRS	FR	IBCH RAS	RU	ER	1	42
3	CNRS	FR	NIIC SB RAS	RU	ER	1	13

[2] The exchange plan foreseen by this Annex I is indicative and can be modified subject to the approval of the REA. However the maximum number of researcher months in the project shall not be increased throughout the duration of the grant agreement.

Participant number	From participant	From country	To participant	To country	Seconded researcher	Duration	Starting month
3	CNRS	FR	NIIC SB RAS	RU	ER	1	18
3	CNRS	FR	NIIC SB RAS	RU	ESR	6	17
3	CNRS	FR	NIIC SB RAS	RU	ESR	2	19
3	CNRS	FR	IBCH RAS	RU	ESR	4	9
3	CNRS	FR	NIIC SB RAS	RU	ESR	3	29
4	FAU	DE	IBCH RAS	RU	ESR	1	35
4	FAU	DE	NIIC SB RAS	RU	ER	2	9
4	FAU	DE	NIIC SB RAS	RU	ESR	2	16
4	FAU	DE	IBCH RAS	RU	ER	1	33
5	UMONS	BE	NIIC SB RAS	RU	ER	2	9
5	UMONS	BE	USYD	AU	ESR	1	10
5	UMONS	BE	USYD	AU	ESR	10	34
6	CIAC	CN	FAU	DE	ER	2	16
7	NIIC SB RAS	RU	IPF DRESDEN	DE	ER	1	10



Participant number	From participant	From country	To participant	To country	Seconded researcher	Duration	Starting month
7	NIIC SB RAS	RU	IPF DRESDEN	DE	ESR	2	22
7	NIIC SB RAS	RU	UNIVIE	AT	ER	1	31
7	NIIC SB RAS	RU	CNRS	FR	ESR	6	30
7	NIIC SB RAS	RU	CNRS	FR	ESR	6	11
7	NIIC SB RAS	RU	CNRS	FR	ER	2	21
7	NIIC SB RAS	RU	CNRS	FR	ER	1	16
7	NIIC SB RAS	RU	CNRS	FR	ER	2	16
7	NIIC SB RAS	RU	FAU	DE	ER	3	12
7	NIIC SB RAS	RU	FAU	DE	ESR	3	10
7	NIIC SB RAS	RU	UMONS	BE	ER	4	8
8	IBCH RAS	RU	UNIVIE	AT	ER	2	15
8	IBCH RAS	RU	CNRS	FR	ESR	5	9
8	IBCH RAS	RU	CNRS	FR	ER	4	9



Participant number	From participant	From country	To participant	To country	Seconded researcher	Duration	Starting month	1																								2																							
								1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
8	IBCH RAS	RU	FAU	DE	ESR	1	25																																																
8	IBCH RAS	RU	FAU	DE	ER	1	25																																																
9	NU	JP	UNIVIE	AT	ER	2	19																																																
10	ZJU	CN	IPF DRESDEN	DE	ER	4	24																																																

5. Project management[3]

In line with article III.2 of the grant agreement a *partnership agreement* will be signed between the *beneficiaries* and the *participant organisations* for the purpose of the *project.* The *partnership agreement* will specify the organization of the work within the network, organize the management of the project, define rights and obligations of the parties, and finally the access to background, the use of foreground publicity and confidentiality. The network respects the fundamental rules of FP7 project intellectual property rights and specifically those expressed in the Annexes II and III to the *grant agreement*.

5.1 Network organization and management structure

Coordination:
The network will be scientifically coordinated by Dr. Anastasia Vyalikh. The coordinator will work together with the WP leaders to ensure the overall cohesion of the project and compliance with the work plan and will act as contact point between WP leaders, the Advisory Board and the Commission. It is assumed that A. Vyalikh will spend up to 25% of her time on the project management and execution.
The local support to the project coordination will be assured at the department of the research planning and –coordination of IPF DRESDEN. Mr. Antonio Reguero will address the issues related to patent application, technology transfer and preparation of research contracts. Mrs. Sandra Martinka appointed as the administrative project manager will provide financial assistance and establish appropriate accounts to record and monitor expenditure.

The scientific and management objectives of the project are organized in 4 Work Packages (WP).

The WP will be guided by the *WP leaders*:
WP 1 *Management:* A. Vyalikh, S. Martinka
WP 2 Synthesis and Functionalisation: E. Flahaut
WP 3 Characterisation and theoretical modelling: C. Ewels
WP 4 Properties investigation and tuning: C. Bittencourt
The WP leaders will monitor the progress of the work programme against the Deliverables and Milestones, improve communication within the WP, assemble the reports from the respective RT coordinators and ensure their compliance with the dead-line.

The Project Management Committee (PMC) will be comprised of the project coordinator and the supervising scientists responsible for the Research Task (RT coordinators). If prevented for any reason, the RT coordinator can nominate another representative of the organization who is concerned with the network activity. The PMC members are:

1. Dr. Anastasia Vyalikh (IPF DRESDEN)
2. Dr. Alexander Grüneis (UNIVIE)
3. Dr. Emmanuel Flahaut (CNRS)
4. Dr. Chris Ewels (CNRS)
5. Prof. Patrice Simon (CNRS)
6. Prof. Vojislav Krstic (FAU)
7. Dr. Carla Bittencourt (UMONS)
8. Dr. Ying Wang (CIAC)
9. Prof. Alexandr Okotrub (NIIC SB RAS)
10. Dr. Lyuba Bulusheva (NIIC SB RAS)
11. Dr. Ekaterina Obraztsova (IBCH RAS)
12. Dr. Stephan Irle (NU)
13. Dr Marcela Bilek (USYD)

[3] The researchers in charge of management activities identified in this section can be replaced by other researchers, and in accordance with the definitions contained in Art. III.1. if they take part in the exchange activities.

14. Dr. De-Yi Wang (IPF)
15. Prof. Hong Fan (ZJU)

Regular meetings (annual) of the PMC will be arranged in order to assess the progress of the work with respect to the Milestones of each WP, to make key decisions, keep the project running and to resolve problems. Decisions are reached unanimously by one vote from each PMC member and all decisions will be made by a simple majority. In the case of equality of the votes, the coordinator will decide. The PMC members will control fulfilling the research tasks, submission of deliverables and Milestones and decide if corrective actions are necessary to reach the project objectives. If for any reason the coordinator is unable to perform her duties, the project shall be managed by the PMC.

The network will establish an *Advisory Board*, which will monitor and evaluate the progress of the research programme and advice future strategies within and possibly beyond the contract period. The Advisory Board members will be informed about the current progress of the work regularly via emails, and will be invited to the network workshops. The board will be comprised of highly experienced professionals from academic science and industry in the fields of bionanotechnology and energy nanotechnology.

Partnership Agreement will be signed by all partners of the network in order to establish the responsibilities and the management structure of the network, as well as to regulate intellectual property rights, patent issues and technology transfer.

The annual network workshops will be organized at the European partner institutions and attended by early-stage and experienced researched involved in the work programme. At the project workshops the progress of each RT will be reported and potential problems and scientific strategies will be discussed. The progress of the work programme will be monitored against the milestones of each WP and compared with the progress of the international state-of-the-art. Financial assistance towards organization of the network workshops will be provided from the internal workshop budget. Investments for this will be negotiated between the partners at the start of the project and decision will be set out in writing in the Partner Agreement. A kick-off meeting of all personnel involved will be held at IPF Dresden at the start of the project. In this meeting, the management structure will be implemented and issues related to administrative and financial aspects will be discussed. The further workshop meetings are planned at the UNIVIE (year 1), IBCH RAS (year 2) and IPF Dresden (year 3).

The participation of the partners from the Third Country organisations in the project will be financed from *Matching Funds* available from the internal sources of the partners from USA and Japan.

Management of incoming seconded personnel: The personnel at the hosting institutions will be in charge of: 1) assisting the incoming personnel with the bureaucratic needs, including those for Visa issuing, if applicable; 2) providing with assistance for accommodations; 3) providing the guest personnel with adequate resources and assistance for carrying out the planned activities and adequate training.

Communication strategy and meetings: The partners will be kept fully informed about the development of the project through a continuous communication process. Daily to weekly communication will be ensured within the staff at the same institution. Communication between the researchers involved in the same WP will be ensured at least weekly through short reports or by making available intermediate results and data (e-mail and web file sharing). Communication between the WP leaders will be ensured through web-conferencing to discuss the scientific activities.

Reporting: A progress reports (technical progress and any deviations from the work plan) will be submitted by WP leaders to the PCM every year. Periodic reports, consistent with EC requirements, will be prepared by the Coordinator on the basis of the reports of WP leaders.

Dissemination of results: The results obtained during this project will be actively disseminated and exploited for the benefits of the actors (individuals and Institutions) throughout the four years cycle of the project. A plan for dissemination will be discussed and managed by the Coordinator and the PSC. Articles published in scientific journals, participation in scientific conferences, public lectures, and the dedicated website will be the principal ways to disseminate results. Both ESR and ER will take part in this process through the presentation of their results during workshop activities, oral lectures, and through manuscript preparation for publication.

Risk Assessment/Contingency Plan: The proposed program is highly ambitious, challenging, and interdisciplinary. However, the feasibility is excellent because of the unique combination of expertise of the participating groups. The decisions concerning any changes in the overall project plan, technical objectives, project management, and for resolving administrative and organisational issues will be taken by the PMC.

5.2 Financial management

The Coordinator holds responsibility for the budget to be properly managed. The members of the management committee will also ensure that the visitor at and from their institution have all the required and appropriate resources (office space, facilities access, housing…). When a specific exchange is not financed by the network, an agreement between both groups in how the living expenses of exchange staff are covered will be settled.

5.3 Secondment strategy

Secondment strategy is organized on the basis of the Gantt chart shown in Table 4. The secondments are organised in three work packages. According to the participants' expertise the exchange scheme is planned in form of training, joint research, joint workshops and seminars.
Every year, the coordinators of all participant institutions will agree on the exchange program and will also ensure that visitors to their institutions have adequate office/lab space allocated for the time of their visit, facilities access, and help with accommodation and travel arrangements.

The main reasons for the choice of the partners are:

- their complementary expertise, adequate for the activities of the project;
- their ability and willingness to collaborate;
- their outstanding record in dissemination and transfer of knowledge, in particular through research publications and education of young generations of chemists;

Roles of seconded Early Stage Researchers, and reasons for their secondments:

- to develop both their laboratory skills and their ability to plan, organize and develop of new ideas in an independent scientific research project
- to widen their scientific perspective through the collaboration with leading scientists
- to improve their communication skills, and their approach to the dissemination of results

Roles of seconded Experienced Researchers:

- to manage the activities of the research group
- to lead scientific discussions, especially with Early Stage Researchers
- to deliver lectures and seminars, and to plan new activities and projects
- to disseminate results through research publications with the partner Institutions.

The duration of secondments is in general one to three months that is reasonable to fulfil the planned work program. Extended visits (up to 10 months) are planned for specific projects parts, which involve developing a strategy to determine the physico-chemistry of the fluorine-based plasma and the resultant fluorination patterns on different carbon materials. The visiting program is organized in such way that the partners involved in the connected tasks or responsible for one deliverable or milestone participate in exchange.

5.4 Intellectual property

A Partnership Agreement, covering issues such as Intellectual Property, will be prepared via e-mail among the coordinators of the network at each institution according to the particular rules of each organization and common use. Bearing in mind that the network is collaborative in nature, and hence it is likely that more than one participant will be involved in generating the knowledge, in order to ensure that no intellectual property is disclosed through publication either in peer-reviewed journals or in conference publications, manuscripts will be circulated to members of the network before publication. Any intellectual property issues that may arise during the network will be reviewed and resolved by consultation with the appropriate support teams of each institution. Patent and Copyright applications will be made where appropriate, in order to protect inventions funded by the network.
In addition, a mediator, appointed among the members of the management committee, will be in charge of resolving any issues of conflict and help to find a consensus in case of disputes. In case of major issues or disputes, the mediator will inform the management committee and decisions will be made by consensus of the management committee team. To reduce potential conflicts, a "Partnership Agreement" has been prepared and this will be finalized and signed if the project is funded. The final version of this memorandum will define the rules of professional conduct within the network, including matters relating to intellectual property rights.

6. Impact

An important new aspect of this proposal is the demonstration of a complete "synthesis-characterisation-device implementation" loop for fluorinated nanocarbon. If such a feedback loop can be established efficiently, the path from discovery to practical consequences will be shortened considerably. The experience gathered in establishing such a feedback loop will be valuable for other areas of energy-related research, where timely transfer of ideas from basic research into technology is of essence.

With distinctive capabilities offered by the involved partners from EU Member States and associated countries, the project will conduct basic and applied research to support ERA's overarching mission to promote scientific and technological innovation and to strengthen Europe's future growth and development. Since speed, effectiveness and efficiency are of essence in developing and commercializing new technologies of the future. Therefore, only joint efforts bringing together EU and national resources, know-how and research capabilities enable achievement of this goal. Regarding the proposed project, the *combination* of the various characterisation techniques available from the project partners and employed in WP 3 provides the comprehensive insight into the structure of the synthesized materials and deep understanding of the fluorination processes. Furthermore, using the different kinds of starting carbon materials (CNT, graphene and graphite) subjected to fluorination by various processing routes (low- and high-temperature synthesis, plasma-based functionalisation) allows to obtain *a wide range of the materials* with different morphology and specific properties, which will be investigated utilizing local facilities of the partners. Thus, analyzing the overall properties (WP 3 and 4) and discussing the obtained results at the project workshops, the *most promising materials* with outstanding characteristics will be selected in order to tune their properties further towards the optimal integration in the next-generation electronics devices, in gas sensing technology or in non-invasive diagnostics in medicine.
Besides scientific benefits, social benefits are also of great importance for the participating researchers. The training at European research facilities at different partner institutions will provide the participants with state-of-the-art knowledge and understanding the importance of communication and cooperation for their professional career's development. Communicating with the researchers from different disciplines and learning different "schools of thought" will open new perspectives on scientific objectivity and approaches. Special efforts within the project will be made to provide training at state-of-the-art experimental techniques in various disciplines for young researchers well beyond what is available at their home institutions or at national levels. This

approach will enhance their career prospects and then provide them with the foundations for an open labor market in EU.

Another significant impact of the proposed partnership is the integration of a gender dimension into the research. Ensuring that 5 principal investigators of 10 participating organisations within the network are female, our consortium supports the EU's gender equality strategy that aims on career progression of female researchers and on increase in leading public sector research positions occupied by women. Thus, involving the female researchers, in particularly, the female project leaders, into the interdisciplinary and trans-national network established within the present project, will strengthen their careers through professional and leadership skill development.

Finally, the present project can serve as a starting point for the organization of a consortium involving European specialists and researchers from other countries, which will be focused on development of efficient and reproducible procedures for large-scale preparation of high-quality novel materials, such as fluorinated nanocarbons. Thus, from the economic and industrial perspective, implementation of the proposed project will ensure a positive long-term economic effect due to development of fundamental grounds for further nanocarbon-based industrial applications and production strategies, as well as a positive environmental effect due to development of new efficient energy generation and storage materials. The establishment of the "NanoCF" network will lead to mutually beneficial research collaboration with researchers from outside Europe making Europe a highly attractive hub in fields of knowledge- and technology-generation. Thus, the outgoing training will enrich the professional experience of the European researchers, whereas incoming highly trained and qualified researchers from outside Europe will increase knowledge sharing through joint-research partnerships and improve the human potential at the European research level.

7. Ethical Issues

This project does not raise any ethical issues.

ETHICAL ISSUES TABLE

	Research on Human Embryo/ Foetus	YES	Page
*	Does the proposed research involve human Embryos?		
*	Does the proposed research involve human Foetal Tissues/ Cells?		
*	Does the proposed research involve human Embryonic Stem Cells (hESCs)?		
*	Does the proposed research on human Embryonic Stem Cells involve cells in culture?		
*	Does the proposed research on Human Embryonic Stem Cells involve the derivation of cells from Embryos?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	YES	

	Research on Humans	YES	Page
*	Does the proposed research involve children?		
*	Does the proposed research involve patients?		
*	Does the proposed research involve persons not able to give consent?		
*	Does the proposed research involve adult healthy volunteers?		
	Does the proposed research involve Human genetic material?		
	Does the proposed research involve Human biological samples?		
	Does the proposed research involve Human data collection?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	YES	

	Privacy	YES	Page
	Does the proposed research involve processing of genetic information or personal data (e.g. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?		
	Does the proposed research involve tracking the location or observation of people?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	YES	

	Research on Animals	YES	Page
	Does the proposed research involve research on animals?		
	Are those animals transgenic small laboratory animals?		
	Are those animals transgenic farm animals?		
*	Are those animals non-human primates?		
	Are those animals cloned farm animals?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	YES	

	Research Involving Developing Countries	YES	Page
	Does the proposed research involve the use of local resources (genetic, animal, plant, etc)?		
	Is the proposed research of benefit to local communities (e.g. capacity building, access to healthcare, education, etc)?		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	YES	

	Dual Use	YES	Page
	Research having direct military use		
	Research having the potential for terrorist abuse		
	I CONFIRM THAT NONE OF THE ABOVE ISSUES APPLY TO MY PROPOSAL	YES	

PART C

8. Overall Maximum Community Contribution

Table 5: Indicative Budget[4]

Participant number in this project	Participant short name	Country	Number seconded researchers month	Total EU Contribution (€)
1	IPF DRESDEN	Germany	14	28,200.00
2	UNIVIE	Austria	15	29,900.00
3	CNRS	France	44	83,600.00
4	FAU	Germany	16	30,800.00
5	UMONS	Belgium	17	34,500.00
TOTAL (€)			106	207,000.00

Table 6: Indicative Secondments[5]

Participant number in this project	Participant short name	Country	Amount of staff	Number seconded researchers month total	% Total	EU Contribution (€)
1	IPF DRESDEN	Germany	4	7	6 %	14,100.00
2	UNIVIE	Austria	3	12	11 %	24,200.00
3	CNRS	France	7	18	17 %	34,200.00
4	FAU	Germany	4	6	6 %	11,400.00
5	UMONS	Belgium	3	13	12 %	26,900.00
6	CIAC	China (People's Republic of)	1	2	2 %	4,200.00
7	NIIC SB RAS	Russian Federation	8	31	29 %	58,900.00
8	IBCH RAS	Russian Federation	4	13	12 %	24,700.00
9	NU	Japan	1	2	2 %	0.00
10	ZJU	China (People's Republic of)	1	4	4 %	8,400.00
11	USYD	Australia	0	0	0 %	0.00
12	TCD	Ireland	0	0	0 %	0.00
13	UCSB	United States	0	0	0 %	0.00
TOTAL EU/AC Participant		6	21	56	52 %	110,800.00
TOTAL Third Country Participant		7	15	52	48 %	96,200.00
TOTAL		13	36	108	100 %	207,000.00

9. Grant agreement reporting

REPORT PERIOD	SCIENTIFIC MID-TERM REVIEW REPORT* DUE AT MONTH	PERIODIC REPORTS** DUE AT MONTH	FINAL REPORT DUE AT MONTH
1	12	**24**	
2	36	**48**	**48**

* According to Articles III.4 of the Annex III of the grant agreement, the beneficiary shall submit for each reporting period a mid-term interim progress report.

** According to Article II.4 of the grant agreement, it includes the activity and management reports and the financial statement (Form C).

The European Union support of Marie Curie Actions will be referenced in publications, conference papers, presentations and posters in connection with this project. This will include the sentence "This research was supported by a Marie Curie International Research Staff Exchange Scheme Fellowship within the 7th European Community Framework Programme", as well as, if relevant, the EU and Marie Curie logos.

[4] This table contains all the beneficiaries and the EU contribution. All of them must submit a Form C for the intermediate payment of reporting period 1 and for the final payment at the end of the project.

[5] This table shows the number of fellow-months per participant. It is an indicative distribution that can be modified because of the project implementation needs. If the changes are not significant it is not necessary the modification of the Annex I but a clear explanation in the due periodic a final report.

ENDPAGE

PEOPLE
MARIE CURIE ACTIONS

International Research Staff Exchange Scheme
Call: FP7-PEOPLE-2013-IRSES

Annex I

“NanoCF”