European Cooperation in the field of Scientific and Technical Research - COST -

Secretariat

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COST 233/09

MEMORANDUM OF UNDERSTANDING

Subject :	Memorandum of Understanding for the implementation of a European Concerted Research Action designated as COST Action MP0902: Composites of Inorganic Nanotubes and Polymers

Delegations will find attached the Memorandum of Understanding for COST Action MP0902 as approved by the COST Committee of Senior Officials (CSO) at its 174th meeting on 26-27 May 2009.

MEMORANDUM OF UNDERSTANDING

For the implementation of a European Concerted Research Action designated as

COST Action MP0902

COMPOSITES OF INORGANIC NANOTUBES AND POLYMERS

The Parties to this Memorandum of Understanding, declaring their common intention to participate in the concerted Action referred to above and described in the technical Annex to the Memorandum, have reached the following understanding:

1. The Action will be carried out in accordance with the provisions of document COST 270/07 "Rules and Procedures for Implementing COST Actions", or in any new document amending or replacing it, the contents of which the Parties are fully aware of.

2. The main objective of the Action is to develop new composite materials from inorganic nanotubes and polymers and to establish appropriate links and transfer of knowledge needed for application and commercialisation of this kind of composite media by European industry.

3. The economic dimension of the activities carried out under the Action has been estimated, on the basis of information available during the planning of the Action, at EUR 84 million in 2009 prices.

4. The Memorandum of Understanding will take effect on being accepted by at least five Parties.

5. The Memorandum of Understanding will remain in force for a period of 4 years, calculated from the date of the first meeting of the Management Committee, unless the duration of the Action is modified according to the provisions of Chapter V of the document referred to in Point 1 above.

A. ABSTRACT AND KEYWORDS

Nanotubes made of inorganic materials are an interesting alternative to carbon nanotubes, showing advantages such as e.g. easy synthetic access, good uniformity and solubility, and predefined electrical conductivity depending on the composition of the starting material. They are therefore very promising candidates as fillers for polymer composites with enhanced thermal, mechanical, and electrical properties. Target applications for this kind of composites are materials for heat management, electrostatic dissipaters, wear protection materials, photovoltaic elements, etc. The Action will link together European scientists working on this rapidly emerging field to create a basis for a highly interdisciplinary research network focused on development and exploration of inorganic nanotube-polymer composites. The action will generate a fundamental knowledge and create widespread links needed for application and commercialisation of this kind of composite media by European industry.

Keywords: Nanotubes and nanowires, inorganic materials, polymers, composites, nanostructured materials

B. BACKGROUND

B.1 General background

The discovery of carbon nanotubes (CNTs) and other new forms of carbon opened a dynamic new field in physics, chemistry, and materials science. Due to their many functional properties CNTs were found to be promising additives to polymeric materials leading to enhancement of various properties of the resulting composites. Fabrication of high quality composites, however, often requires very pure starting material, good particle dispersion, and-at least when enhanced mechanical properties are desired-strong adhesion between particle guests and polymer host. These requirements still pose great difficulties for CNT composites. For these reasons synthesis of alternative filler particle types, in particular inorganic nanotubes and nanowires, becomes increasingly important.

During the last decade it was demonstrated that formation of fullerene-like and nanotube structures is not specific to carbon, but is a generic property of (2D) layered materials, such as WS_2, MoS_2, etc. Very interesting nanotube and nanowire forming materials are transition metal/chalcogen/halogenides, described by the formula $TM_6C_yH_z$ (TMCH), where TM is transition metal (Mo, W, Ta, Nb), C is chalcogen (S, Se, Te), H is halogen (I), and the composition is given by $8.2<(y+z)<10$. TMCH tubes can have a subnanometer-diameter, lengths tuneable from hundreds of nanometers to tens of microns, and are functionally similar to CNTs, but in contrast to their carbon-based counterparts, they exhibit a profoundly good homogeneity and solubility of the raw material. Their excellent dispersiveness is due to extremely weak mechanical intertube coupling. Other properties with potential for applications include very good field-emission properties, an anomalously large paramagnetic susceptibility, and promising electronic characteristics. The properties of TMCH and other inorganic nanotubes in composites with polymers are at the moment practically unexplored. The first attempts of making polymer composites with the TMCH nanotubes have revealed an order of magnitude improvement of the mechanical strength of cellulose fibers by adding only 0.1 wt% of the TMCH additive, while measurements of electrical conductivity of poly(methyl methacrylate) (PMMA) films doped with TMCH nanotubes revealed a percolative bahaviour with an extremely low percolation threshold.

As the research of inorganic nanotube-polymer composites is just in its starting phase, it is still too early for a targeted EU proposal. The number of European research groups active on the topic is at present relatively small and there is little scientific interaction between them. But, on the other hand, there are many European groups having a widely recognised expertise and experience in research of CNTs and their composites. The main idea of the Action is hence to link groups with knowledge on synthesis and characterization of TMCH nanotube materials with groups that have experience in fabrication of polymer composites with CNTs and/or other additives and their characterization. This will contribute considerably to the coordination of interdisciplinary research efforts across Europe needed to gain knowledge on fundamental features of inorganic nanotube-polymer composites. Such a coordinated Action is prerequisite for application and commercialisation of this kind of novel composite media as well as for basic understanding of their physical properties.

The main benefits of the Action will be:

1) further improvement of the synthesis of TMCH and related nanotubes and nanowires with extremely high uniformity and purity and optimisation of their solubility in various polymer hosts by appropriate functionalisation,

2) determination of correlations between nanotube content in a polymer matrix and the electrical, optical, thermal, and mechanical properties of the resulting composites,

3) development of different methods for nanotube alignment in the polymer host and optimisation of the associated macroscopic anisotropy of the composite medium,

4) development of theoretical models suitable for description of nanotube-polymer composites and prediction of their structure-property relationships,

5) testing and evaluation of the new composite materials in view of predetermined properties regarding specific applications.

The Action will open up a promising new topic for advanced scientific and technological exploration of nanostructured materials. COST offers by far the most appropriate framework for this Action, as it aims to bring together the existing expertise from different national initiatives in the larger EU-region to study the potential of inorganic nanotube polymer composites for novel and enhanced materials. The Action will foremost provide a platform to combine this existing knowledge and to identify common issues and problems. It will then bundle the expertises and pave the way for development of new materials in view of different properties and applications. Because of the very early stage of the present research activities on the topic, other frameworks, such as ESF, EUREKA or the EU Framework Programme are at the moment still not suitable. However, the Action will lay the foundations for future collaboration and enable the interested teams to take the next step towards applying for joint research projects under the scope of these frameworks.

B.2 Current state of knowledge

During the last two decades there was an explosion of research on nanowires, nanotubes and similar one-dimensional (1D) molecular systems associated with exceptional electronic, magnetic and mechanical properties. The extremely large aspect ratio of these systems implies strongly 1D behaviour. At present CNTs and their variants are definitely the most explored 1D materials. Unfortunately, manufacturing CNTs with predetermined properties is still practically impossible at present, and their functionalised versions are typically not conducting, which is limiting their usefulness in sensors and molecular electronics devices.

Considering inorganic compounds, it was demonstrated that layered MS_2 materials (where M denotes metals like Mo, W, etc.), can be grown in the form of nanotubes. Nanotube materials of various kinds were synthesised by different strategies, e.g. chemical vapour transport, use of solid template, sulfidization, etc. Their availability in macroscopic amounts allowed systematic studies of their properties and possible applications. Investigations of the mechanical properties have shown that some of those nanotube materials exhibit Young's moduli almost as high as that of CNTs (TPa range). In-situ tensile and buckling experiments were carried-out on individual WS_2 tubes by using SEM and AFM tips as a probe. The observed strength with respect to the Young's modulus was found to be exceedingly high in comparison to conventional high strength materials. Optical spectroscopy studies of the MS_2 nanotubes revealed their semiconducting nature. Intercalation of lithium (Li) and hydrogen (H) into nanotube structures was investigated in view of their energy storage capabilities, and promising values of the discharge capacity were revealed. Considering tribological properties, it was demonstrated that MS_2 nano materials have large potential for applications as solid lubricants in car industry and aerospace as well as in medical, home appliances and numerous other sectors. Recently the production of MS_2 nanotubes was scaled-up to a commercial level, which makes these materials now available to all kinds of industrial needs.

Very interesting similar inorganic 1D systems are also nanotubes and nanowires of transition metal/chalcogen/halogenides (TMCH), such as for instance $Mo_6S_{4.5}I_{4.5}$. It was demonstrated that, conversely to CNTs, and conversely to MS_2 nanotubes, TMCH nanowires exhibit one-type all-metallic behaviour, are dispersible in common solvents and tend to debundle in solution. As was recently shown, this makes them ideal candidates for conductive fillers for various kinds of composites. Besides electrical conductivity, TMCH nanotubes display also many other fascinating physical and chemical properties that make them promising for applications such as wear resistant materials, lubricants, pressure, temperature and chemical sensors or indicators, etc. The properties of TMCH nanotubes and nanowires are thought to be sensitive to the stoichiometry of the material, which could be controlled by adjusting the synthesis conditions. Therefore tailoring the materials properties for selected applications seems to be feasible as well as essential for commercialisation of the TMCH nanotube-polymer composites.

Most of the synthetic routes leading to TMCH nanostructures were originally developed and patented in Europe. A recent manufacturing technology breakthrough enabled easy and efficient synthesis of pure TMCH nanotubes and nanowires in macroscopic quantities. This opened up a possibility for extensive investigations of pure nanotube materials as well as of their various composite media. It is hence feasible and also essential for the European Research Area (ERA) to keep its leading role and competitiveness in this field with respect to other industrial countries, such as Japan and USA. This requires an immediate programme of concerted scientific collaboration between different European countries. Thus COINAPO, which is aimed at providing coordination of relevant research efforts across Europe, is very appropriate and timely to keep Europe on the leading edge of research and exploration of the TMCH nanotube-polymer composite media.

Multifunctional materials based on composites of polymer and inorganic nanotubes are designed at the nanoscale and are expected to have great impact in the future. The properties of TMCH and other inorganic nanotubes in composites with polymers hold great potential for applications, yet, they are at the moment still practically unexplored. The key innovation of this Action is development and exploration of new composite materials merging the specific properties of TMCH nanotubes and nanowires with the widely recognised versatility and suitability of polymer media. This opens up an unexpected range of possible applications to be explored in the future. The prerequisite needed to achieve this goal is bringing together scientists from different research fields and representatives from various innovative technology sectors.

B.3 Reasons for the Action

The main reason for launching this timely Action is the fast progress of a European laboratory in synthesis and purification of TMCH nanotube materials and successful starting of their commercialisation via a spin-off company. This company now provides macroscopic quantities of nanotube materials, which opens up a possibility for broad-range investigation of their properties. The COINAPO project will link together European scientists with critical expertise in the fabrication and characterisation of nanocomposites. During the project, the fundamental science of the interaction between the TMCH material and the polymer host in novel nanocomposites will be studied in detail and suitable theoretical models will be developed to describe their response. The cumulative effort will help improve fundamental understanding and also control the properties of the formed nanocomposites. By the end of the project it will be possible to provide European researchers reliably with nanocomposites tailored to specific mechanical, optical and electro-photonic applications. At its onset, COINAPO has the potential to address several economical and scientific needs and by the end of the project this potential will be assessed. Under the umbrella of this COST Action the critical mass required to advance the field and also support further funding and exploration activities will be established.

The main objectives are:

A) Understand the structure of the produced TMCH nanotubes and their solid state characteristics,

B) Develop methodologies for dispersing these materials within polymers,

C) Study the structural, opto-electronic and mechanical properties of the nanocomposites,

D) Determine the effect of processing on the final properties of the TMCH material and of the nanocomposites,

E) Model the response of the material as means to deeper understanding and optimisation of material.

F) Establish characterization protocols for determining the key properties for key applications of TMCHs in polymer composites as these will be identified through consortium meetings and workshops.

The main means are:

A) Follow existing expertise in large scale production of the TMCH nanotubes,

B) Use a plethora of structural characterisation techniques including nanometre probes such us surface probe microscopy, electron microscopy, x-ray and neutron scattering, etc.,

C) Investigate the mechanical and thermal properties of the material by means of UTM, DMA, DSC, and different special techniques,

D) Investigate the variation in electrical and optical response of the material depending on concentration and orientation of the nanotubes. Proposed methods include DC and AC conductivity measurements, Raman, IR and UV/VIS spectroscopy, polarising optical microscopy, ellipsometry, non-linear optical techniques, etc.,

E) Importantly, research will be coordinated to optimise impact and the involved scientists will meet regularly to exchange ideas and decide future directions.

The Action is principally aimed at European scientific/technological advance. Its focus will be on development of new materials with improved mechanical, thermal, electronic, and optical properties. On the other hand, it is obvious that innovative new materials with fine-tuned properties for selected applications, such as energy storage, mechanical protection, medical instrumentation, etc., can have large potential impact also for progress of economic and societal needs.

The main aim of the Action is a broad-range collaborative research effort and exploration of a new type of nanostructured materials. As the principal part of the activities will be R&D activities directly aimed at creating new fundamental knowledge, the main deliverables of the Action will be research reports that will be disseminated to the public in the form of scientific publications in refereed international journals, as chapters in textbooks, and as presentations at international meetings. Patent applications will also be considered, when appropriate. Possibly also a few demonstrator-like prototype devices will be manufactured. Public engagement will be facilitated by articles in non-specialised journals and "away days" in schools. Many different topics will be studied by various research teams following different paths with respect to the materials selection, use of experimental and theoretical techniques and properties studied. Instruments available within the scope of COST Actions such as short term scientific missions, workshops and narrowly focused conferences offer excellent opportunities to find common interests between different research teams and disciplines, resulting in widening the merit of the project and research potential to develop further international collaborative projects (e.g. 7th European Framework Program). The Action will offer an open framework of collaboration, which will encourage participation of research teams from the industrial sector and the sharing of pre-competitive information. Finally, the results and conclusions of the Action will be used by ERA policy makers to identify future priority themes and by evaluators to judge the potential of future proposals in this area.

B.4 Complementarity with other research programmes

To the best of our knowledge there are only two running EU projects partially related to research of TMCH nanostructures. These are:
FOREMOST (FP6) (http://www.euprojekt.su.se/index.php/kb_69/io_1285/io.html), and
COMEPHS (FP6), http://www.comephs.com/).

As research on composites of these particles with polymers is at the moment in its birth phase, commercialisation oriented programmes such as EUREKA or specific priorities within the FP7 are at present not suitable for the networking Action.

Another partially related project was NANOTEMP, which was a Research Training Network funded by the European Commission's 5th Framework Improving Human Potential programme. The network contract HPRN-CT-2002-00192 was signed between the European Commission and network participants on 01/10/2002 with duration of 48 months. The NANOTEMP project was dealing with the preparation, characterization, modification and handling of nano-structures in particular carbon nanotubes and inorganic fullerenes.

This COST Action is also partially related to the running COST Action MP0701: "Composites with novel functional and structural properties by nanoscale materials", which is considering polymeric composites with “classical” nanoparticles, such as ceramic, metallic and similar nanoparticles. On the contrary, this Action will be focused on particular kind of the nanocomposite materials based on novel type of nanoparticles - namely TMCH nanotubes and nanowires. Due to the profound 1D nature of this nanoparticles the large part of activities will be devoted to problems, such as for instance various techniques for nanoparticle alignment and related composite anisotropy, which have no analogy in “classical” nanocomposite materials.

C. OBJECTIVES AND BENEFITS

C.1 Main/primary objectives

The main objective of the Action is to create a highly interdisciplinary network focused on research and development of new composite materials from inorganic nanotubes and polymers and to establish appropriate links and transfer of knowledge needed for application and commercialisation of this kind of composite media by European industry.

C.2 Secondary objectives

The Action will identify promising composites with a set of improved properties, such as thermal, mechanical and electronic properties, which will allow them to be used successfully in a variety of industrial applications. Furthermore, health, economic and ecological issues will be taken into account during the evaluation. The Action will provide a cooperative basis for interdisciplinary research that is necessary to fulfil the primary aim and will allow a growth of general knowledge in the field of Inorganic Nanotube - Polymer (IN-P) composites. A study of these materials from a fundamental point of view is necessary in order to assess their applied aspects. Coordinated research of different European research groups will result in a broadening of the impact of any new knowledge obtained, as current fundamental research in this promising field is quite limited. The participation of partners from industry will facilitate the transfer of knowledge and will ensure that feedback can be provided to the research Action.

Coordinated activities will be focused on synthesis and fabrication of new IN-P composite materials with structure-tailored properties to match the needs of selected applications (e.g. heat dissipaters, electrostatic dissipaters, wear protection, photovoltaics, actuators) and on characterization and understanding of their chemical and physical properties by using a variety of experimental and theoretical approaches.

To summarise, the secondary objectives are:

1) transfer of people and knowledge between different European research groups in order to speed up the progress of fundamental research as well to assess the suitability of the studied materials for new and existing applications.

2) attain a wider involvement with partners from eastern European countries; up to now a relatively small number of partners from eastern Europe is involved in COINAPO.

3) establishing interdisciplinary links between physicists, chemists and material scientists working in the field.

4) identifying possible wide scale cooperative work in the future and applying for joint research projects within the 7th EU Framework Programme.

5) establishing a link to European industry and stimulating development and implementation of IN-P composites in areas such as nanoelectronics, thermal management and photovoltaics.

C.3 How will the objectives be achieved?

The starting activity needed to attain the primary objective of COINAPO will be to allocate research groups in Europe, which have expertise in the field of nanostructured composite media and are interested in participating to investigations of composites of inorganic nanotubes with polymers. A critical mass of researchers from different fields with different backgrounds needs to be attained. 32 research teams from 21 COST countries have already expressed their interest for participation, while the ultimate goal of the Action is to reach at least 50 partners from 25 COST countries. This will be achieved by advertising the Action at international meetings and exhibitions, via web page of the Action and on local web pages, via various e-mailing lists, within scientific magazines and via collaborative contacts between individual researchers. The initial event of the Action will be a big kick-off meeting in which the Working Groups, the Management Committee and other formal bodies of the network will be established. This activity will possibly take place during a large multidisciplinary European conference such as E-MRS in order to maximize the exposure of the network among European researchers and industry. The basic concepts, plans and information workshops on available infrastructure will be discussed. After this, regular topical meetings and workshop will be organized on a yearly base.

Special efforts will be put on attracting the partners from companies (at present 13% of the consulted teams interested in participating to the Action are from SMEs). For this purpose at least one topical meeting will be organized with emphasis on the dissemination of the results to industry. Representatives from selected SME's and large industrial laboratories in Europe will be invited, as well as a specialist from the European Patent Office, who will be contacted for advice whenever necessary. The generation of valuable IP will be an important aspect in the long term and will generate licensing opportunities and spin-off potential. Emphasis at meetings and workshops will be also on active participation of the young researchers whose creativity is essential for achieving the objectives of the Action and who will benefit strongly from it in terms of training and a rapid establishment of an exchange of people and knowledge with industry and importantly with SME's.

Experience and information between the partners will be exchanged via the regularly updated network website (password-coded for network partners only), which will be established in addition to the standard COST website of the Action.

C.4 Benefits of the Action

The technical relevance of IN-P composites makes this field promising for the development of new materials with unique properties and applications. Exploratory research is quickly evolving worldwide. Yet, activities of European groups working on the topic and/or exhibiting interest for it are at the moment quite scattered. Meetings on a regular basis will help correlate the work of European researchers and enhance their potential to succeed in designing novel materials and applications along this route. Complementary expertise and research interests of different groups will be linked together. Many researchers working on nanotubes are young scientists, who will greatly benefit from short-term scientific missions and interaction with leading workers from other research groups. The Action is expected to have a considerable scientific and also technological benefit for the know-how in this emerging research field in Europe.

At the end of this COST Action a wide set of new IN-P composite materials will be available with well known thermal, mechanical, electronic and optical properties. Synthetic routes will be optimised in view of low-cost production of macroscopic quantities of the best materials suitable for specific applications. Theoretical models will be developed to explain the observed features and to provide a basis for tailored development of new composites. This will make Europe a leading area in the R&D of the IN-P composite materials.

Research in the Action will take place within a consortium with the critical mass and complementary expertise to support the participants in terms of basic knowledge transfer and management of their efforts. In addition to the consortium partners, major beneficiaries include the wider society through the creation of wealth and the ERA due to critical knowledge created.

C.5 Target groups/end users

Cooperation and contacts will be established with innovative European sectors and technological incubators developing advanced products based on using novel promising materials. The Action will protect Europe's interests and inventions in the area of IN-P composite materials and will spin new ideas and activities out into start up companies and SME's, and ultimately to larger industrial companies. It will give European manufacturers a market lead over strong competition from Japan, China and the United States.

Cooperation will be established also with normalization and standardization bodies. Realising the goals of this COST Action will provide a sound base for setting completely new quality and reliability standards for a wide range of composite materials and methods for monitoring/controlling specific processes.

Extensive contacts will be established with various scientific institutions. Target groups for the Action are both experienced researchers and young scientists involved in the development of composite materials with improved electrical, mechanical, thermal and optical properties. The Action will provide the opportunity for Academic Institutions as well as Industry to participate and coordinate their research efforts on a European level, which will be important for the advancement of R&D in polymer composites research.

In addition to the particular application of IN-P composites, the knowledge and understanding gained in this COST Action will be of such generic nature, that it will also be relevant to other branches of nanotechnology and materials science. The Action will contribute greatly to the strong position of the universities and research institutions involved in the field of nanomaterials and polymer research dealing with the interrelations between structure, chemistry and mechanical (and functional) properties of multi-materials systems. This will make these academic institutions more attractive for industrial (commercial) partners oriented towards sustainable technologies and operations relevant for the long-term needs of society and will help them maintain a strong position in international networks.

Furthermore, it is important for university academics to work at the cutting edge of materials science addressing globally important issues in order to maintain the educational standards of European students at a high level.

D. SCIENTIFIC PROGRAMME

D.1 Scientific focus

The Action will address the following research tasks:

1) Chemistry and Materials Science

Chemistry oriented partners will on the one hand focus on improving synthesis methods, the main goal being to increase the yield and uniformity of the nanotubes and nanowires, on the other hand on the design and preparation of the composites with suitable polymers. A broad library of different preparative techniques will be utilized to find optimal end materials. Materials scientists will also be responsible for the detailed structural characterisation of the produced material.

2) Physics

Partners with background in basic scientific research will concentrate on mechanical, electrical, thermal and optical properties. This will give feedback on the progress of the efforts during the fabrication of the IN-P composites. Several experimental investigative techniques will be employed to allow not only determination of the macroscopic properties but also examinations of the nanoscale structure, in particular regarding dispersion quality (minimum bundle size) and nanotube/wire orientation. The results will constitute most important feedback for the further efforts in the Chemistry task. The structural and electronic characterisation at the nanoscale will very likely require the use and development of innovative analytical methodologies and sample preparation techniques.

3) Engineering

Engineering-oriented partners will define a few selected application areas where IN-P composites will be competitive and whose realization can be foreseen in the near future, at least on a prototype scale. Demonstrators or prototype materials and devices will be developed and compared to existing alternatives in industrially relevant tests. The results will be fed back to all partners with the aim to optimise all relevant processing stages, materials used etc. in order to improve the materials/devices.

4) Theory

Different mesoscale modelling and computer simulations will be used to explain/predict the properties of investigated composites and to decide on the most promising directions for their further improvement in view of selected applications. Micromechanical models, percolation models and various molecular dynamics simulations will be exploited for predicting the material properties. Temperature, nanotube type and nanotube volume fraction and orientational order will be used as control parameters, just to name a few.

A particular bonus of the Action is that the aims of its research programme can only be met via strong interactions in a multidisciplinary team of scientists, which in turn requires an EU wide research base. The human and technical means to achieve the objectives of the Action are the availability of key researchers with interdisciplinary/complementary expertise and access to complementary facilities for meetings and workshops at different locations in Europe and also their accessibility for "on-line" consultation via the Action web site. This will enhance the exchange of ideas and consequently increase productivity of all the network partners.
Scientific progress in all areas broadly described above will be reinforced by timely feedback from various tasks. Meetings and workshops within the COST Action are the best vehicle for feedback delivery, cross-fertilization of ideas and transfer of crucial knowledge.

D.2 Scientific work plan - methods and means

The innovative research on IN-P composite materials will be focused on two different aspects: preparation of characterization of polymer nanocomposites as well as systematic investigations of their potential in view of applications. Such studies will inspire new theoretical concepts, experimental realizations (physical and chemical approaches), novel characterization techniques and possible commercialisation of IN-P composite materials for use in practical devices. This Action will promote an effective pan-European cooperation and thus support a fast and promising development in this challenging field.

The Working Groups will focus on the following objectives

1) WG1 ("Fabrication of materials") objectives:

   A) Synthesis of TMCH nanotube materials and their functionalisation

   New quasi-one-dimensional $TM_6Ch_yH_z$ materials will be systematically synthesized in a single step procedure using variable reaction conditions and different educts (halogens, chalcogens, metals). Various substitutions, e.g. selenium replacing sulphur, will be tested to form nanowires. Synthesized nanowires will be used as a precursor material to obtain novel nanotubes and peapods of transition metal dichalcogenides via sulphurisation. This route will provide large amounts of starting material for producing composites. In addition to TMCH nanotubes some part of research efforts will be focused also on WS_2 and similar nanotubes. Different functionalisation methods, such as ultra sonification and melt mixing, will be investigated in order to improve solubility of the nanotubes in polymer hosts. Techniques like non-covalent functionalisation of the nanotube sidewalls by the use of phthalocyanines, ruthenium bipyridyl, or pigmented cyanides will also be evaluated. The latter adsorb strongly on highly oriented pyrolytic graphite forming well-ordered arrays.

B) Design of composites with polymers and nanotube/nanowires material

A notable advantage of TMCH nanotubes is their efficient dispersivity (ability to easy debundle) in organic solvents such as ethanol, benzene or toluene. This is essential for achieving optimum percolation and surface contact area with the polymer matrix and thus controlling composite physical properties. Exfoliation and dispersion of nanotubes in aqueous media using suitable surfactant salts followed by deionisation and solvent exchange into organic solvent will also be tested. Introduction of nanotubes into various polymers, commercial as well as research grade, either via dispersion directly in the polymer or via pre-dispersion will be investigated. Liquid crystal polymers and polymerisable low-molar mass liquid crystals will be also studied as possible hosts. Samples for further characterization will be prepared by different fabrication technologies, such as e.g. electrospinning, fibre spinning, vapour deposition, and in-situ injection molding.

C) Testing of the safety of the composites

All new composite materials will be tested for their innertness/inflammability and other basic chemical properties. Homogeneous and heterogeneous inorganic fullerenes or other nanomaterials will be incorporated in the nanotubes. Nanoparticles created in this way are protected against release into the atmosphere avoiding some potential health risks. The peapod structure represents a promising technology for the safe production and transport of nanomaterials with preserved original size distribution.

D) Structuring of the composites

Various methods for thin film deposition (spin coating, dip coating, etc.) of the composite material will be investigated. Nanostructured films suitable for glass and flexible substrates will be prepared by various chemical methods in order to be incorporated as e.g. the transparent conducting electrode in organic optoelectronic devices. Particular attention will be paid to the correlation of the theoretical and real performance of the films in comparison with the commercial available indium tin oxide (ITO) films in terms of sheet conductivity and optical transparency. Furthermore, the nanostructures will be dispersed in highly conductive thiophene derivates, such as PEDOT/PSS and evaluated. Different methods for nanotube alignment within the polymer network will be examined: flow alignment, unidirectional mechanical and/or thermal treatment, application of external electric/magnetic field, photo-polymerisation with linearly polarized light (LPP), use of liquid crystalline polymers, etc. Lyotropic liquid crystalline suspensions will be prepared from the TMCH particles, similar to those which have been made using well-dispersed CNTs at high concentration, and which can be further processed into fibers with excellent mechanical properties due to the spontaneous alignment of the nanotubes.

Short term exchange visits (STSM) of scientists active in WG1 to groups active in WG2 will be stimulated to exchange knowledge on material preparation and manipulation procedures and to establish valuable interlinks between chemists, physicists and material scientists.

2) WG2 ("Characterization") objectives:

A) Structural characterization of the composites

To study the nanowire atomic structure and their structural defects leading edge electron microscopy techniques, such as high resolution electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) will be used together with conventional techniques (TEM, AFM, etc.). These techniques will be applied also to determine the microstructure of the formed nanotubes within the composite, their dispersion in polymer matrix and interface properties between the nanotubes and polymer. Composites will be analysed by X-ray (SAXS) and neutron scattering techniques at various conditions, like temperature (cryogenic facilities), applied external electric field or stress, etc.. This will provide information on volume fraction, spatial arrangement and alignment of the nanotubes in the polymer matrix. Structural properties of the composite and its alignment and anisotropy will be studied by spatially-resolved micro-Raman spectroscopy. Electron paramagnetic resonance spectroscopy (EPR) will be used to characterize radical polymerisation reaction in composites in combination with in-situ optical excitation of photo-induced polymerisation. Advanced methods, such as High Angle Annular Dark Field (HAADF) imaging will be used to determine the position of dopant atoms and elucidate their effect on the properties of nanotubes.

B) Characterization of mechanical properties

Universal testing machine (UTM - determination of Young's and shear modulus, tensile strength, etc.), dynamical mechanical analysis (DMA) and rheometry will be used to resolve stress-strain properties and to allocate the linear and nonlinear regimes in the mechanical response of the composites. Measurements with different directions of applied force will be performed to resolve possible elastic anisotropies of the material. Time dependent stress/strain analysis will be performed to study possible non-recovery phenomena. Time resolved optical techniques with sub-picosecond resolution (e.g. optical Kerr effect) will be used to investigate fast local vibrations and slow structural dynamic processes.

C) Characterization of thermal properties

Temperature dependence of structural and physical properties will be studied. Various phase transitions will be determined via differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) measurements, with particular interest in glass transition temperatures (Tg). The value of Tg is essential for the selection of materials for various applications. The effect of degree of cross-linking/branching of the polymer on glass transition temperature will be studied.

Thermal conductivity and thermal diffusivity will be measured. Time-resolved techniques (e.g. impulsive transient grating experiments) will be used to investigate acoustic/elastic properties, structural rearrangement and thermal diffusion phenomena in relation with the local nanostructure of the material.

D) Characterization of electrical properties

Electrical (I-V) measurements will be routinely used to investigate the evolution of a percolation network of the nanotubes within the composites as their concentration increases. Chemical analysis at the nanoscale will be carried out using STEM to explore the change in electronic properties and variation in bonding due to chemical treatment of the nanotubes. Dielectric spectroscopy will be used to determine AC current properties depending on temperature, frequency and composition. Tensoresistance will also be investigated and field emission properties will be tested. In view of applications in solar cells the composites will be sandwiched between a metal anode and a transparent ITO (Indium-Tin Oxide) cathode on glass. The associated measurements will cover: complete characterization of the solutions from which the active layer is formed, the study of the homogeneity of the photoactive composite layer (morphological and opto-electronic properties); the precise determination of the photovoltaic parameters in correlation with the open environment conditions; and the exploration of efficient sealing materials and techniques.

E) Characterization of optical properties

Conventional optical analysis (refractive index, birefringence, optical absorption measurements) and optical spectroscopy (Raman, IR, UV-VIS, ellipsometry, fluorescence, etc.) will be used to resolve optical properties of the composites. Optical holographic techniques will be employed in view of possible applications of the IN-P composites in optical information processing and also for characterization of the alignment-induced local anisotropy. Electro-optic, elasto-optic and/or nonlinear optical properties will be investigated, such as frequency conversion and waveguide characterization. Hyper-Rayleigh and hyper-Raman scattering will be used for nonlinear optical (NLO) characterization. Charge transport in relation with photoluminescence will also be investigated. Nonlinear refractive index of the composites will be analysed in view of all-optical switching applications. Various studies on possible photonic applications of the composites in large-scale-integrated photonic devices will be made.

Short term exchange visits (STSM) of scientists active in WG2 to other WGs will be stimulated within the Action to broaden and deepen the knowledge of especially young scientist with their origin from different scientific disciplines.

3) WG3 ("Theory") objectives:

A) Development of basic theoretical models
Existing theoretical frameworks for CNT-polymer composites will be taken as starting point and optimised and/or modified for the case of TMCH-polymer composites, for instance with respect to the guest-host interaction strength in these composites, and for identifying the optimum usages of composites containing single-wall tubes, multi-wall tubes and nanowires, respectively. Mechanical properties of the composites will be analysed in the frame of micromechanics (composite-) models and percolation models. Temperature, nanotube type and nanotube volume fraction and orientation order will be used as control parameters.

B) Modelling of structure-property relationships
Charge transport, heat transport and optical properties will be investigated in these essentially one-dimensional systems, including linear and nonlinear effects. In connection with the question of nonlinear effects and transport properties, the possible existence of solitonic solutions will be examined. Finally, the effect of the reduced dimensionality will be investigated.

Short term exchange visits (STSM) of scientists active in WG3 to groups active in WG2 will be arranged within the Action to correlate various theoretical models with most important experimental problems and findings.

4) WG4 ("Engineering") objectives:

New composites will be developed with tailored material properties leading to improved thermal conductivity for thermal management (e.g. for heat dissipation for computer chips), improved electrical conductivity (e.g. for the use as electromagnetic-interference shielding and electrostatic dissipation), improved mechanical properties (e.g. for applications as wear protection), and improved linear and non-linear optical properties (e.g. for optical communication networks) and strong exciton dissociation at the bulk heterojunctions (organic solar cells), as well as new promising materials for large area flexible multifunctional sensors that could be integrated into the material and can be used for multiple location sensing. An example of practical motivation is for instance to consider the use of smart sensors *in-situ* ability to detect symptoms of potentially catastrophic events of vehicles in real time.

Testing of these new composite materials will be made in strong cooperation with partners from industry as well as from research institutes and academic bodies (see Section E.2: Working Groups).

E. ORGANISATION

E.1 Coordination and organisation

COINAPO will last for 4 years. It will strengthen and stimulate the basis for building scientific excellence in Europe by linking groups of different expertise to an interdisciplinary network, especially for young scientists. All activities will be supervised by the Management Committee (MC) aiming at planning, coordinating and evaluating work actions. A project manager will be designated to take care of every day business.

The Management Committee (MC) of COINAPO will be organized and run according to "COST Rules and Procedures for Implementing COST Actions".

The MC will ensure active interaction and effective information transfer between the groups. All research work of participating groups will be carried out and funded by national financing schemes with COST providing just a coordination of the Action. In the course of the Action new partner groups beneficial to the network will be located and invited to the network with the purpose to reach the critical mass of research capacities needed to make Europe a leading research area in the field of nanotube-polymer composites.

The MC will also establish the Working Groups (WG) and assign their Coordinators. Initially three WGs will be launched, which will build the scientific basis of the Action. Together with the WG Coordinators the MC will prepare detailed work plans for specific activities of the Working Groups and financial plan to adequately share the resources within the Action budget. Follow up activities will also be planned in correlation with milestones listed below. The members of the MC and the WG Coordinators will convene twice per year and will critically evaluate the present phase of the Action and define optimal ways of execution of further phases.

Milestones:

Year 1

A) First preparation of IN-P composites.

B) First characterisation of material properties of IN-P composites.

C) Evaluation of existing theories.

Year 2

A) Preparation of the 2nd series of IN-P composites.

B) Characterization of material properties of the 2nd series of IN-P composites.

C) Start of development of new theories.

Year 3

A) Final selection of most promising composites and preparation methods thereof.

B) Testing of optimised materials for some selected applications.

C) Development of new basic theoretical models.

Year 4

A) Map of different IN-P composites materials properties.

B) Final evaluation of IN-P composite structure-property-relationship.

C) Demonstration of the first prototype devices based on IN-P composites.

All research groups will be strongly encouraged to participate in topical meetings and workshops to promote the optimal exchange of ideas and information, especially between researchers from academic institutions and those from industry. In this way it will be possible to keep all participants continually informed about the status of the Action and to stimulate new research directions if and when necessary.

In case that several groups from the same European country will participate in the network, a national coordinator of the Action will be appointed. He/She will prepare a plan of specific national activities, such as exchange visits between the laboratories and organization of short meetings on a national basis. These activities will be initiated in consultation with the MC of the Action and the national COST representative.

A web manager will be appointed to coordinate the activities needed to establish an Action specific website and take care that it will be regularly updated on a monthly base. Two kinds of information will be available: password protected internal information aimed at sharing the ideas and experience between the partner groups and open information aimed at dissemination and exploitation of the results of the Action to the target groups such as Academia, Industry and other public domains. The COINAPO website will also provide an interactive form to attract other partners interested to join the Action.

E.2 Working Groups

The Action will be organized initially in 3 Working Groups: WG1 - "Fabrication of materials", WG2 - "Characterisation", and WG3 - "Theory". After the first year of the Action a fourth Working Group will be launched. This WG4 will focus on possible applications of the new composite material (WG4 - "Engineering"). The MC will decide about formation and appropriate reorganization of the existing WGs, as soon as initiatives or needs appear to split the activities into more Working Groups.

WG1 - "Fabrication of materials"
will focus on developing and optimising methods for tailoring the structure and properties of the composites and their constituents (on their own as well as in the mixed state). The most appropriate and/or interesting materials will be prepared in quantities large enough for systematic investigations in various laboratories. Standardisation of the synthetic routes and IP management (patenting), when appropriate, will be arranged.

WG2 - "Characterisation"
will focus on determination of the actual structure and physical, optical, and electronic properties of the composites as well as their constituents. Different experimental facilities will be used according to the plans for extensive complementary research on the material properties. The group will disseminate wide-scale info on physical properties of different composites to all partners.

WG3 - "Theory"
will develop fundamental understanding of the composite properties on the basis of theoretical models and computer simulations. Models of the structural, optical and electronic properties of the composites will be developed by different approaches.

WG4 - "Engineering"
will focus on the testing and evaluating of the new composite materials regarding specific applications such as e.g. heat dissipaters, electrostatic dissipaters, wear protection materials, photovoltaic elements, and development of related prototype-style samples/devices.

A Coordinator will be appointed for each Working Group to coordinate the work within the group and represent the activity on the MC. The scientific programmes will be carried out in close cooperation with other WGs and strong overlap between the members of these groups is expected in all fields of interest. This participation of individual researchers in more than one Working Group is encouraged to enhance information exchange between different groups.

E.3 Liaison and interaction with other research programmes

The MC will actively seek to cooperate within other international projects, organized both under EU patronage and by other bodies (industrial, professional, committees etc.). The MC will search for and invite leading academic and industrial colleagues in various subjects to give plenary talks during annual workshop meetings and joint seminars.

One partner of the Action has just been funded by the FP7 (Marie Curie Intra-European Fellowship scheme) with a proposal based on the structural characterisation of MoSI nanowires and WS_2 nanotubes. The knowledge attained within the MC Fellowship scheme will serve as a valuable base for her active involvement in the Action.

Active interaction will be established with the COST Action MP0701: "Composites with novel functional and structural properties by nanoscale materials". This Action is focused on research of nanocomposite media in general, which means that specific knowledge on IN-P composites that will be attained within the Action can importantly broaden the scope of the Action MP0701. On the other hand, exchange of experience on other types of nanocomposite media gained within the Action MP0701 can be very helpful for progress of the Action. A joint workshop of both Actions will be organized to stimulate the information exchange.

E.4 Gender balance and involvement of early-stage researchers

This COST Action will respect an appropriate gender balance in all its activities and the Management Committee will place this as a standard item on all its MC agendas. The Action will also be committed to considerably involve early-stage researchers. This item will also be placed as a standard item on all MC agendas.

Gender issues:
By its nature, the content of the work foreseen in COINAPO, is gender-neutral and does not require a specific analysis of the impact of the work on any particular social group. It is however essential, that the partners, through their work, ensure that all social groupings are encouraged to participate in the programme, particularly those that have been traditionally under represented in this scientific field. In this way, the consortium can significantly contribute to the achievement of the ERA in promoting gender equality as described previously.

The COINAPO Gender Action plan will be developed along two main objectives:

1) To ensure gender equality within the consortium,

2) To encourage young female scientists to take up careers in the research dedicated to composites based on inorganic nanotubes and polymers and to promote the role of women in such areas not only in academia, but also at industrial level.

The WG coordinators will have, as part of their set objectives, the tasks of encouraging the participation of women in the management and implementation of the Action (to ensure a balanced representation is achieved) and the resolution of any gender-related issues that arise. The MC will be responsible of monitoring that all Action steps are performed under a 'same equality of chances for men and women' basis. Currently, 5 women have been identified to participate actively in this COST Action as possible members of the MC.

Involvement of young researchers:
The Action will provide an extensive platform for education, re-education, training, and development of entrepreneurial skills. In order to remain competitive in advanced and emerging technologies, Europe also needs scientists in a wide range of disciplines, who have the ability to look over the narrow confinement of their own disciplines. Another benefit of creating a multidisciplinary Action is the enhancement of cultural exchanges between EU scientists, and the training aspects of young researchers who will inevitably get together to give a new generation of scientists with a common pan-European experience and outlook.

At workshops and topical meetings organized within this COST Action a number of young researchers will always be invited to present their work in an oral presentation, depending on the scientific quality and originality of their contribution. This will provide them with a possibility to acquire the skills needed for public speaking, which are very important at large international meetings. Some time will be devoted also to round-table discussions on open problems related to the topic. The PhD students and other young researchers will necessarily participate at these events, as such sessions offer an excellent possibility for them to get trained in scientific communication with their peers. This activity will strengthen the transfer of knowledge from the experienced researchers to the younger ones and consequently foster the realization of their capacity building. A special training school for young researchers considering the activities of all Working Groups will be organized in the 3rd year of the Action.

F. TIMETABLE

The Action will last for four years. Within six months after the start of the Action the general targets and timetables for the full Action period will be agreed between the 3 WG and the MC, and a detailed plan of the Action will be added as information to the MC. At the end of the first year the procedure for formation of the fourth WG, namely WG4-"Engineering", will be discussed by the MC and, if necessary, appropriate rearrangements of the other WGs will be planned. The detailed workplan of the WG4 will be made. Contributions from each WG to the annual report should be made against these documents. During the whole Action the MC will take proper measures to promote optimal synergy between the programmes of the separate WGs.

The MC will organise 4 Action workshops covering all research activities involved, one start-up meeting, one midterm review during the Action and one final meeting before drafting the final report. The MC will be proactive in also organising joint seminars - preferably across the WG borders - where and when relevant. The main tasks of the Start-up meeting include finalising details of the WGs R&D focus and the preliminary timetable of the Action.

The following events/activities will take place:

1) Start (kick off meeting): beginning of Year 1.
2) Formation of WGs 1,2 and 3: first half of Year 1.
3) Formation of WG4: first half of Year 2.
4) WGs Meetings: one meeting in the middle of each year, Year 1 - Year 4.
5) MC Meetings: one meeting in Year 1, two meetings in Year 2, two meetings in Year 3, two meetings in Year 4.
6) Topical meetings and workshops: one meeting in the second half of each year, Year 1 - Year 4.
7) Training school for young researchers: End of Year 3.
8) Scientific exchange programme: at all times during the course of the Action.
9) Information exchange: at all times during the course of the Action.
10) Reports: end of each year, Year 1 - Year 4.
11) Mid-term evaluation: end of Year 2.
12) Final Evaluation and Report: End of Year 4
13) End of the Action: public event at the end of Year 4.

G. ECONOMIC DIMENSION

The following COST countries have actively participated in the preparation of the Action or otherwise indicated their interest: AT, BE, CY, CZ, FR, DE, GR, IE, IL, IT, LV, LT, NL, PL, PT, SK, SI, ES, SE, CH, UK. On the basis of national estimates, the economic dimension of the activities to be carried out under the Action has been estimated at 84 Million € for the total duration of the Action. This estimate is valid under the assumption that all the countries mentioned above but no other countries will participate in the Action. Any departure from this will change the total cost accordingly.

H. DISSEMINATION PLAN

H.1 Who?

The dissemination plan addresses two target audience groups, internal and external ones. The internal dissemination is obvious and will be realised trough the regular activities of the Action described above and below (workshops, meetings, website, etc.). The external dissemination will address the following main bodies:

A) Industrial (commercial) bodies,
B) Academic or research institutions,
C) Young researchers,
D) General public,
E) Other related research frameworks,
F) Industry associations.

The industrial target can be quite broad and will be related to composite materials in general. This includes materials with enhanced electrical, mechanical, thermal, optical, and sensing properties for many different applications, such as e.g. materials for heat management, electrostatic dissipaters, wear protection materials, photovoltaic elements, just to name a few. Another target audience are researchers in general working in an industrial or academic environment in the field of polymer nanocomposites. Due to this broad range of application fields the MC will prepare and update regularly a list of potentially interested commercial and academic institutions to provide them with updated information about recent developments of composite materials for selected applications.

H.2 What?

The dissemination methods intended to be used are:

A) Publication of general information on relevant public websites, directing visitors to the COINAPO website,
B) Positioning of working documents on the COINAPO website, partly freely available and partly on password protected pages,

C) Additionally to the COINAPO website: an electronic communication network (e.g. an internet discussion forum),

D) Publications: state of the art reports, interim reports, case study reports, proceedings, guidelines, manuals, final reports,

E) During events such as e.g. workshops, seminars and conferences organised by the MC, contributions to other national and international conferences and symposia,

F) Publications in peer-reviewed scientific and technical Journals,

G) Non-technical publications in general press,

H) School visits and engaging with young people to display how fascinating science is.

H.3 How?

The dissemination of results will be used by various routes:

A) The main route to the dissemination of results will be *via* articles published in peer reviewed journals as well as oral presentations at key related conferences; participation at which this Action will encourage. This will include also scientific journals of a more general nature. All publications arising from research carried out under this COST Action will credit COST support, and the MC will encourage and promote joint publications.

B) A second important route to dissemination of results will be the annual topical workshops aimed at discussing the progress achieved to date and to bring together researchers from academia and from industry. The MC will encourage and invite scientists not involved in this COST Action to broaden and deepen knowledge of different topics related to the Action.

C) An interactive internet web site will be created shortly after the start of the Action to disseminate the information among the participants and also to the public. Therefore, public and password protected sections of this webpage will be established to allow proper exchange of knowledge, publications, reports, meeting schedules, contact points for researchers, job openings and other information.

D) An internet discussion forum and an E-mail contact-network will be installed among the participating researchers, from universities, institutes and industry.