Polymer Nanocomposites Based on Inorganic Fullerene-like WS₂ Nanoparticles: Opportunities and Challenges

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Polymer-based composites were heralded in the 1960s as a new paradigm for materials. By dispersing strong, highly stiff fibres in a polymer matrix, high-performance composites could be developed and tailored individual application. Today, we stand at a similar threshold in the realm of polymer nanocomposites because in all major industries, there is an acceleration of the longstanding unfulfilled demand for lighter, stronger, and more affordable materials with low nanofiller content. However, the continuous progress has been hindered because the disruption of the low-dimensional crystallites (eg. tactoids, bundles, agglomerates) to achieve uniform distribution of the nanoelement (eg. layered silicate, single wall carbon nanotube and carbon fullerenes, respectively) continues to be a challenge.

Novel strategies such as the dispersion of inorganic fullerene-like tungsten disulfide (IF-WS₂) nanoparticles offer an attractive means to combine the merits of organic and inorganic materials into novel nanocomposite systems. The IF-WS₂ nanoparticles do not require exfoliation or modification, making it possible to obtain stronger, lighter materials without the complexity and processing cost associated to these treatments. Here we focus in the opportunities and challenges in the use of these kinds of nanoparticles in order to prepare new formulations of novel polymer nanocomposites, as a lightweight alternative for use in automotive, aerospace, transport and various industrial friction and wear components. The prime objective of this research is to develop and characterize novel polymer nanocomposites processed by advantageously traditional melt processing technique. Different types of polymeric matrices were tested ranging from high-performance polymer systems to commodity semicrystalline thermoplastics [1-5]. It well known that the properties of a crystalline polymer including the thermodynamic, physical or mechanical ones depend on the details of the structure and morphology that evolve from the melt. Thus, detailed nanolevel investigation along with the performance evaluation would give insight into the structure–property–performance relationship of such nanocomposites.

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Influence of the Size, Morphology, Structure and Cristallinity on the Tribological Properties and the Lubrication Mechanism of IF-MeS\textsubscript{2} (Me=W, Mo) Nanoparticles

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The use of nanoparticles as additives of lubrication is more and more considered in tribology. They are considered as environmental-friendly and offer a real alternative to classical phosphorus and/or sulfur containing lubricants. Increasing number of articles have reported superior anti-friction and anti-wear performances of these nanoparticles. Most of these research activities focused on carbon based nanoparticles (nano-onions, nanotubes, nanodiamonds, ...), boron nitride nanoparticles, or inorganic fullerenes (IF) of metal dichalcogenides as IF-MoS\textsubscript{2} or IF-WS\textsubscript{2}. These latest are currently among the most studied. Their tribological properties can sometimes be exceptional. Different synthesis routes exist to obtain IF nanoparticles. Depending on the process and by adjusting the synthesis parameters (temperature, reaction time, annealing, ...) it is possible to obtain particles of different size, morphology and cristallinity [1-2]. These parameters influences strongly the lubricating properties of the nanoparticles. In this paper, we will compare the tribological properties of WS\textsubscript{2} and MoS\textsubscript{2} inorganic fullerenes obtained using two distinct synthesis routes and we will try to establish a correlation between the size, the morphology, the number of layers, the degree of cristallinity of IF nanoparticles and their tribological properties.

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Novel Techniques for the Preparation of Transition Metal Chalcogenides

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Transition metal chalcogenides were synthesized by all four techniques employed in my laboratory for the synthesis on nanomaterials. The methods are 1) Sonochemistry, 2) Microwave dielectric heating, 3) Sonoelectrochemistry, and 4) RAPET (Reaction under Autogenic Pressure at Elevated Temperatures).

Special attention will be devoted to the DMS (diluted magnetic semiconductors) such as $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ their synthesis and their magnetic properties.

Lately, we have tried to prepare a layer by layer ZnSe/C/CdSe/C composite by the conducting a step by step RAPET reaction. Instead, we have obtained Zn$_x$Cd$_{1-x}$Se/C core/shell nanocrystals with 31-39 nm semiconducting core and 11-25 nm carbon shell.

If time will permit, I will discuss the preparation of nanosized metal fluorides and illustrate their antibiofilm activity against gram positive and gram negative bacteria. The metal fluorides were coated by our technique on a flat glass surface. This effort is not continued in coating Catheters enabling them to stay in the human body for more than 24-48 hours, which is the current practice.

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Electronic Devices with Dichalcogenide Nanolayers

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We have exfoliated single layers from a number of dichalcogenide materials using the micromechanical cleavage technique commonly used for the production of graphene. Optical microscopy together with AFM was used to characterize the nanolayers and establish optimal conditions for rapid identification of monolayers using optical methods.

We have also electrically contacted nanolayers using electron-beam lithography and fabricated field-effect transistors. Our devices have high on/off ratio and show that dichalcogenide nanolayers could be interesting for nanoelectronic applications.

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Recent Developments in the Fields of Clay Mineral Nanotubes and Zn_{1-x}Fe_{x}O Nanoparticles

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While traditional transition metal chalcogenide and halide nanostructures have made their progress from fundamental research to first applications, clay mineral nanotubes have only been revisited recently [1-3]. Most remarkably, these tubes show properties which are unknown in the world of nanotubes so far, in particular when referring to the family of imogolite and its derivatives: Single-walled nanotubes have a well-defined diameter and also a quite well-defined length [4, 5]. Substitution of Si by Ge yields Ge-imogolite [2], which can be produced easily and in large quantities in the laboratory. Ge-imogolite is somewhat thicker and shorter than imogolite, but also exhibits a well-defined diameter. Surprisingly, double-walled Ge-imogolite nanotubes have just been discovered [3], and they are again nearly monodisperse. Many of the physical properties, as well as potential applications, of these new materials are yet to be explored. I will review this field in the first part of my presentation.

In the second part, the alloying of ZnO nanoparticles with Fe will be discussed. Recent results indicate that one can form Zn1-xFexO nanoparticles with x reaching about 0.2 without significantly changing the lattice structure [6]. Moreover, Fe is quite homogeneously distributed over the particles. We will discuss the implications of these results on metal oxide based nanostructures.

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Chevrel Phases: Amazing Chalcogenide Materials and Interesting Cathode Materials for Rechargeable Mg Batteries

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We report herein on the syntheses of Chevrel phases (CP) based on the following compositions: \( M_xMo_6S_8 \) and \( M_xMo_6S_{8-n}Se_n \) where \( M = \text{Li, Mg, Zn, Cu, Ni, Cd, Na, Pb, Mg+Cu} \) and more. We discuss herein their unique structure which allows their fast electrochemical intercalation reactions with a large variety of metal cations, including multi-valent cations. The solid state diffusion aspects and the population of insertion sites in CPs as a function of the size and charge of the intercalating ions will be discussed. It was discovered that \( Mo_6S_8 \) and \( Mo_6S_{8-n}Se_n \) intercalate reversibly with Mg ions to form \( Mg_xMo_6S_8 \) and \( Mg_xMo_6S_{8-n}Se_n \) \((0 < x < 2)\). We also discovered a fast electrochemical reversible displacement reaction in which Mg ions can interact with \( CuMo_6S_8 \) and extrude copper out thus forming \( CuMg_xMo_6S_8 \). The relatively fast reversible Mg ions insertion into these compounds, made them to be very attractive cathode materials for rechargeable Mg batteries. We will demonstrate R&D efforts toward development of rechargeable batteries with CP cathode materials and will outline directions for further developments in this field, based on our understanding of the correlation among structure, morphology & electrochemical performance.

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Nanotechnology has reached the stage of development where not individual nanoparticles but rather systems of greater complexity are the focus of concern. These complex structures incorporate two or more types of materials, an example of which is the formation of metal-semiconductor hybrids, which effectively combine the properties of both components. The first challenge is to assemble the nanomaterials into a complex hierarchical or supramolecular system. Nanotubes (NT-MQ$_2$) and nested fullerenes (IF-MQ$_2$) of layered metal chalcogenides are inorganic analogues of carbon fullerenes and nanotubes consisting of metal atoms sandwiched between two inert chalcogenide layers. The steric shielding of the metal atoms by the chalcogen surface layers from nucleophilic attack by organic ligands makes chalcogenide nanoparticles highly inert and notoriously difficult to functionalize.

We have devised new and chemically specific methods for the immobilization of metal oxide nanoparticles onto the surface of WS$_2$ nanoparticles [1]. The modification strategy is based on the chalcophilic affinity of the transition metals based on the Pearson HSAB concept. As some chelating ligand are more potent anchor groups for 3d metals than the sulfur atoms of the chalcogenide nanoparticles, the metal oxide nanoparticles can be further functionalized to tailor the chalcogenides surfaces at room temperature or reversibly detached from the chalcogenides surfaces with an excess of the ligand.

Furthermore, progress has been made by employing chalcophilic transition metals in combination with multidentate surface ligands [2]. The 3d metals “wet” the sulfur surface of the chalcogenide nanoparticles while the multidentate surface ligands partially block one hemisphere of the metal thereby preventing an aggregation of the chalcogenide nanoparticles through cross-linking. This strategy for the assembly of aggregates relies on two strategies. The first is to attach bifunctional organic linker molecules to pre-synthesized nanoparticles and then to use them to attach functional molecules or a second type of nanoparticles. We have used this approach to conjugate chalcogenide nanoparticles with porphyrins and metalloporphyrins which, upon photoexcitation, undergo electron transfer followed by the generation of a charge-separated species.

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Recognition of the Atomic Coordination in Multiwalled Inorganic Nanotubes by Means of Atomic-Resolution TEM

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Nanotubes are one-dimensional nanostructures and unlike crystals with three-dimensional periodicity the direct imaging of single atoms with the transmission electron microscope (TEM) is complicated. Previous reports on the crystallographic coordination of MoS\textsubscript{2} microtubes and nanotubes based on electron diffraction experiments indicated a stabilization of the rhombohedral 3R polytype in microtubes and 2H polytype patches in nanotubes [1]. Strictly spoken the order is local and it is hardly possible to use the bulk 2H-phase and 3R-phase stacking terms when closed low dimensional nanoparticles or nanotubes are concerned, since the individual layers are no longer free to move relative to each other.

In this work a comparison between experimental and simulated atomic-resolution TEM images is used to overcome complications with direct image interpretation in order to determine the local coordination of M (M=W or Mo) and S atoms in nanotubes and exfoliated layers. Images were calculated for a number of model structures and compared with experimental data. Under certain conditions the discussion can be limited to the alignment of parallel or antiparallel S-M-S linear or chevron patterns. The comparison between experiment and simulation indicates a predominance of a local coordination corresponding to the 2H and 3R bulk phase of MS\textsubscript{2}, but there is also indication of the trigonal 1T coordination. The analysis further gives information on the chirality of the outer shells of the nanotubes. In agreement with ref. [2] only small chiral angles were observed for the outer shells.

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Structural Characterisation of Two-Dimensional Atomic Crystals

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The discovery of graphene produced through micromechanical cleavage of graphite has opened up a path towards production and investigation of 2D nanomaterials prepared using top-down approach. Similar to graphite, other layered materials such as hexagonal boron nitride (hBN) and transition metal dichalcogenides (TMCs), can be cleaved down to single flakes. 2D layers of these materials have wide range of electronic properties, extending from semiconductors to metals, which explains the particular interest towards them. However micromechanical cleavage cannot provide simple, high-yield preparation method for 2D nanomaterials. The only reasonable alternative method is liquid-phase exfoliation which surprisingly can be achieved in common solvents. However it will give nanosheets with different number of layers present. The aim of this work is, starting with hBN, tungsten disulfide (WS2), and molybdenum disulfide (MoS2), to develop electron microscopy analysis method which can be used to determine exfoliation state of the platelets in the solution. Based on the results obtained, the exfoliation procedure can be optimized in order to achieve maximum possible number of nanosheets with small number of layers present in the solution. Aberration corrected electron microscopy is applied to observe the atomic structure of the exfoliated platelets. An additional, much simpler, characterization procedure will be discussed based on the intensities of the diffraction spots of individual nanosheets.

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Electromechanical Characterization of Carbon and MoS$_2$ Nanotubes via Objective Molecular Dynamics

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In spite of the great interest, microscopic modeling of chiral nanotubes and of nanotubes under mechanical torsion has been challenging. We show that replacing with helical symmetry the standard translational symmetry incorporated in the standard first principles methods is the key to efficiently account for the interplay between the classical ionic and electronic degrees of freedom in nanotubes with arbitrary chirality and twist.

We exemplify how the linear and nonlinear elastic response of carbon nanotubes in torsion was derived using our symmetry-adapted method called objective molecular dynamics [1] (MD). All the important nanomechanical details, such as critical strain beyond which nanotubes behave nonlinearly, the most favorable rippling, and the twist- and rippling-related changes in band gap, are now identified from a solid atomistic basis. We will focus on understanding the way in which rippling, the development of helicoidal furrows and ridges, affects the electronic states. The intralayer strain rather than the known bilayer-coupling effect, dominates the gapping of metallic tubes. Surprisingly, a new effective strain concept allows relating the electromechanical response of the complex rippling state to the behaviour of flat graphene.

With objective MD, chiral NT structures can be computed in a nanomechanical way, as the result of the Eshelby's twist introduced by the axial screw dislocation, Fig. 1. This enables [2] the surprising revelation of a large catalog of MoS$_2$ nanotubes that lack the prescribed translational symmetry and exhibit chirality-dependent electronic band-gaps and elastic constants. Helical symmetry emerges as the natural property to rely on when studying quasi-one dimensional nanomaterials derived via screw dislocations.

Figure 1. An armchair metal sulfide nanotube (lower) under an axial mechanical glide (black arrows). This leads to an axial Eshelby's twist (red arrow), and a change in chirality (upper).

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Stacking and Registry Effects in Layered Materials: The Case of Hexagonal Boron Nitride

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The interlayer sliding energy landscape of hexagonal boron nitride (h-BN) is investigated via a van der Waals corrected density functional theory approach. It is found that the main role of the van der Waals forces is to "anchor" the layers at a fixed distance, whereas the electrostatic forces dictate the optimal stacking mode and the interlayer sliding energy. A nearly free-sliding path is identified, along which bandgap modulations of ~0.6 eV are obtained. We propose a simple geometrical model that quantifies the registry matching between the layers and captures the essence of the corrugated h-BN interlayer energy landscape. The simplicity of this phenomenological model opens the way to the modeling of complex layered structures, such as carbon and boron nitride nanotubes.

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Electronic Properties of $n$- and $p$-doped MoS$_2$ Nanotubes

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Recent progress in the chip generations and the growth of computational facilities cannot go beyond the current strategy of integrated circuits based on semiconductors. As a possible way to overcome in the near future the limitations of widely spread photolithography could be more extensive development of circuits, which would be based on layered compounds and their tubular forms. The most attractive candidates are $d$-metal sulfides such as MoS$_2$ and WS$_2$ due to their high chemical resistance and good mechanical properties. The preservation of the electronic properties by change from the bulk to the nanotubular state was proved only for pure compounds [1].

Here we present the results of quantum-mechanical calculations within density-functional tight-binding scheme for MoS$_2$ monolayer and nanotubes doped by Nb, Re, Ti in metal and I in non-metal sublattices. The general picture of a change in the electronic structure is identical to that for many other bulk semiconductors. $p$-doping (by Nb or Ti) causes a slight splitting of half-occupied electronic level from the valence band, while $n$-doping (by Re and I) causes a splitting of half-occupied level from the conduction band into band gap of MoS$_2$ (see Fig.). Finally, the doping with Re atoms is considered in more detail depending on the concentration of dopant, size and chirality of nanotubes and compared with available experimental data [2].

![Figure 1. Molecular orbitals’ energies near Fermi level for (14,14)MoS$_2$ nanotube doped by single Re atom and their visualizations demonstrate a strong localization of the dopants level.](image)

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2. R. Tenne (private communication)
Theoretical Investigations on the Formation and Structure of AgI Nanocrystallites by Encapsulation in Carbon Nanotubes and Carbon Nanotubes Junctions.

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Besides the possibility of creating intrinsically monodimensional materials through nanotube-driven template syntheses, one of the most interesting aspects of encapsulation concerns the formation of ordered structures in the hollow of carbon nanotubes (CNTs), in the form of nanocrystallites. The one-dimensional confined growth of different compounds has been viewed as a suitable route to the development of new low-dimensional materials, like nanowires. In recent experimental studies metal halides were inserted into the nanotube hollow in excellent yields. In this work, the morphologies of AgI nanocrystallites grown inside \((n,n)\) single-walled CNTs and CNTs junctions are investigated by means of molecular dynamics simulations.

All crystal structures found are formally constituted by \((n,m)\) AgI nanotubes, with chiral vectors \(n\) and \(m\) depending on the CNT diameter and on the local environment. In particular, for narrow CNTs unprecedented low-dimensional AgI nanoribbons appear. In larger diameter CNTs, inorganic \((n,m)\) AgI nanotubes are typically formed. Hence, the filling of large diameter CNTs can eventually lead to the concurrent formation of different AgI aggregates giving rise to a scenario of polymorphism in the nanoregime.

As a further assessment we analyze the possibility to simulate the growth of monodimensional nanocrystallites of AgI inside CNTs junctions. Interestingly new inter-phase structures, which allow the transition between different AgI phases, are observed in the region of the CNTs junctions.

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Probing the Atomic-Scale Details of Molecular Adsorption on MoS$_2$ and CoMoS Nanoclusters by STM

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The ability of the Scanning Tunneling Microscope (STM) to resolve the atomic-space realm of matter has made it possible to address the detailed edge structure of single-layer MoS$_2$ nanoclusters, which contain the active sites for hydrotreating reaction. I will demonstrate how we can resolve molecular adsorption on the edges of MoS$_2$ and a range of promoted CoMoS-type structures synthesized on a gold model substrate by means of high resolution STM images. The STM studies reveal that both unpromoted MoS$_2$ and CoMoS nanoclusters adopt edge “brim” structures that are significantly electronically and geometrically reconstructed compared to the bulk-truncated forms of MoS$_2$ nanoclusters. To elucidate the role of the particular CoMoS and MoS$_2$ edge structures in hydrotreating reaction, we have investigated the chemical bonding to a number of relevant S- and N-containing probe molecules. Detailed insight has been obtained on the importance of the modified electronic structure and undercoordinated sites, and we have resolved the configurations in which the molecules preferably interact at these sites. In particular, we have been able to address the atomic-scale origin of inhibition effects caused by N-containing molecules, which are directly visible in STM images to selectively block the active sites on the nanocluster edges.

Figure 1. Atom-resolved STM images of a small MoS$_2$ nanocluster showing formation of S vacancies and subsequent adsorption of dibenzothiophene (DBT) on corner sites

Furthermore, we have thoroughly elucidated the fundamental adsorption selectivity of MoS$_2$ nanoclusters towards the group of refractory dibenzothiophenes (DBT). Interestingly, we report a pronounced size-dependent chemical affinity for direct adsorption of DBT, which is induced by structural edge changes also observed in the STM studies of the smallest MoS$_2$ structures [1]. The atomic-scale observations of molecular adsorption on both unpromoted and promoted MoS$_2$ model catalysts correlate well with observed activity parameters for the technical catalyst, but the new detailed atomic scale insight also suggests that improvements may be realized by an enhanced control of the nanocluster morphology in the hydrotreating catalysts.

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**Torsional Stick-Slip Behavior in WS$_2$ Nanotubes**

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We experimentally observed atomic-scale torsional stick-slip behavior in individual nanotubes of tungsten disulfide (WS$_2$) [1]. When an external torque is applied to a WS$_2$ nanotube, all its walls initially stick and twist together, until a critical torsion angle, at which the outer wall slips and twists around the inner walls, further undergoing a series of stick-slip torque oscillations (Figure 1). This is contrary to what happens in a multi-wall carbon nanotube, where an external torque causes only the outer wall to slip and twist smoothly around the inner walls. We present a theoretical model based on DFT-based calculations, which explains the torsional stick-slip behavior of WS$_2$ nanotubes in terms of a competition between the effects of the in-plane shear stiffness of the WS$_2$ walls and the inter-wall friction arising from the atomic corrugation of the interaction between adjacent WS$_2$ walls.

![Figure 1](image)

Figure 1. (a) SEM image of a WS$_2$ nanotube-pedal device used to twist individual WS$_2$ nanotubes. (b) Schematic of the AFM experiment and stick-slip behavior. (c) Torque-torsion curves for several press cycles for one device (nanotube diameter $d = 22$ nm). (d) Torsion angle versus time obtained from a SEM movie of a WS2 NT ($d = 24$ nm) twisting due to static charging.

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Graphene Analogues of MoS\textsubscript{2} and WS\textsubscript{2}

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Graphene analogues of MoS\textsubscript{2} and WS\textsubscript{2} have been prepared by chemical methods which include intercalation of lithium followed by exfoliation, reaction of molybdic acid or tungstic acid with excess of thiourea at high temperatures in a nitrogen atmosphere. Products of these reactions examined by microscopic techniques show that they contain one to three layers of MoS\textsubscript{2} or WS\textsubscript{2}. Raman spectra show softening of the A\textsubscript{1g} and E\textsubscript{2g} modes in these few-layer materials. The same behaviour is observed in samples prepared by micromechanical cleavage of crystals as well. Density functional calculations predict the occurrence of larger gap in single-layer MoS\textsubscript{2} and softening of phonons compared to bulk material. Discovery of the two-dimensional graphene analogues of MoS\textsubscript{2} and WS\textsubscript{2} fills the gap that we have had in the family of nanocarbon analogues which had till now zero-dimensional fullerenes and one-dimensional nanotubes. We now have inorganic analogues of nanocarbon in all three possible dimensions.

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Recent Progress in MoSI Nanowires

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Individual MoSI NWs have exceptionally low coupling to the environment and to each other, which leads to one-dimensional quantum electronic transport behaviour. NW bundles with different diameters reveal systematic power-law dependence of the conductivity on temperature and voltage. This suggests tunnelling through Tomonaga-Luttinger liquid segments, in some cases modified by environmental Coulomb blockade from defects.

Scale-free self-organized critical networks such as the human brain show resistance to failure and fast signal processing. MoSI NWs self-assemble into hybrid networks with gold nanoparticles. The length distribution of the edges in the network shows a strong power-law tail, contrary to the log-normal length distribution of the individual wires. This shows that the self-organized critical behaviour is not a property of the NW synthesis, but of their self-assembly into networks.

MoSI NWs in liquid dispersion show a clear correlation between the bundle diameter distribution (obtained by statistical evaluation of TEM images) and the optical absorption spectrum; the absorption peaks shift from 1.8 to 1.5 eV and from 2.7 to 2.4 eV with increasing bundle diameter. The structure of the peaks is analyzed as a function of diameter, suggesting that either the material is intrinsically heterogeneous or that doping plays a crucial role in bundling. Our empirical finding is a breakthrough for nanowire wet processing, since it tremendously speeds up the characterisation of dispersions.

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Intercalated Halogen Molecules as Radiative Centers in Transition Metal Dichalcogenide Layered Compounds

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Transition metal dichalcogenides (TX$_2$), due to their layered structure, can be intercalated with foreign atoms and molecules that change electronic properties of those materials [1]. This work investigated radiative properties of WS$_2$, WSe$_2$, MoS$_2$ and Mo$_{1-x}$W$_x$S$_2$ compounds intercalated with halogen molecules.

Single crystals were grown by chemical-vapor method, using iodine, bromine and chlorine as transport agents. The steady-state and time-resolved photoluminescence measurements were made in the temperature range $T=2\div150$K.

The sharp-lines photoluminescence, observed at low temperatures located at the energies of ~ 0.1eV lower than the indirect band gap, is shown to be produced by bound excitons related to the transport agent, intercalated in 2H-TX$_2$ crystals during the growth process. The diatomic halogen molecules, unambiguously positioned in the adjacent tetrahedral sites of the van der Waals gap, yield neutral centers, providing an efficient radiative recombination.

Beside the excitonic emission caused by halogen impurities, a structured IR luminescence broad band associated with an intrinsic defect (deep center) of the 2H-TX$_2$ host lattice was detected for all samples, including natural molybdenite and synthetic crystals grown without transport agents. The recombination of the excited carriers via these defects is treated as a shunt channel for excitonic emission.

A kinetic model is proposed to describe the recombination processes taking place in the halogen-intercalated 2H-TX$_2$ crystal. The fast thermal quenching of the sharp-lines emission at $T>50$K is accounted for by the self-trapping of the bound excitons. The simulation, carried out in the frame of the kinetic model using the experimentally determined lifetime and energy values of the excitonic states, shows a good agreement with the observed characteristics of the steady-state and time-resolved luminescence.

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Large-scale Synthesis of TaS\textsubscript{2} Nanotubes from Ta\textsubscript{2}O\textsubscript{5} Nanotube Templates

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The discovery that layered transition metal dichalcogenide materials such as WS\textsubscript{2} and MoS\textsubscript{2} could form nanotubes and other inorganic fullerene–type structures has generated considerable interest in nanomaterials consisting of two-dimensional, layered structure. Control over the nanoscale architecture could also greatly accelerate investigations of finite size effects on complex electronic properties such as superconductivity and charge-density wave (CDW) behavior. For example, tantalum disulfide (TaS\textsubscript{2}) displays three polytypes where Ta atoms are covalently bonded between two layers of S atoms in trigonal prismatic (2H), octahedral (1T), or mixed (6R) coordinations. Investigations of structure-property relationships of TaS\textsubscript{2} nanomaterials have been limited, however, because they can neither be produced in high yield nor with control over the crystalline structure.

This talk will describe how large quantities of multi-walled TaS\textsubscript{2} nanotubes can be synthesized from Ta\textsubscript{2}O\textsubscript{5} nanotube templates in a gas-phase reaction. This synthetic route can achieve control over the length, diameter, and the number of TaS\textsubscript{2} layers in the nanotube. Significantly, these nanotubes exhibit electronic properties very different from their bulk counterparts, including an elevated superconducting transition temperature as well as a suppressed CDW transition temperature. The structural control demonstrated by our method is important for the study of fundamental electronic properties of materials in reduced dimensions.

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Novel Non-Coherent Optics for Generating Nanomaterials by Photothermal Ablation

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This presentation will cover the development and demonstration of new, efficient, pragmatic optical methods for the synthesis of a variety of inorganic fullerene-like nanomaterials, based on ultra-bright non-coherent (non-laser) light from the sun and from new generations of short-arc discharge lamps. Successful case studies include: cage-like nanostructures of Cs₂O, fullerene-like and nanotube MoS₂ and WS₂, nanowires and nanospheres of SiO₂ generated for the first time from pure quartz, nanorods of pure Si, and more. Some of these nanostructures even achieved fundamentally minimum sizes predicted by molecular structural theory. Our novel optical systems create the type of non-equilibrium strong-gradient reactor conditions conducive to the production of these metastable nanostructures.

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The MoS$_2$ Nanotubes and Products of their Exfoliation

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Recently discovered the first inorganic nanopods [1] have led to an enthusiastic synthesis of a variety of possible morphologies of nanoparticles grown in a confined geometry of nanotubes. A simple temperature control of morphology, size and inner structure of nano hybrids leads to a selective morphology like coaxial nanotubes, “mama”-tubes [2] with encapsulated nano-onions, the growth of MoS$_2$ nanobuds or it facilitates a release of MoS$_2$ nano-onions, which then form weakly bonded self-assemblies. [3]

A relatively low temperature (873 K- 1073 K), which enables a slow release of iodine leads in general to a formation of MoS$_2$ nanotubes composed of several coaxial cylinders showing a high concentration of structural defects. Nanotubes keep an outside shape of the precursor Mo$_6$S$_2$I$_8$ nanowires. Difference in mass density between Mo$_6$S$_2$I$_8$ and MoS$_2$ compounds leads to a creation of an empty space inside the MoS$_2$ nanotubes. In a case of MoS$_2$ nanotubes this empty space separates the adjacent cylinders and enables an easy diffusion of iodine and molybdenum compounds during the transformation process, which proceeds from outside towards inside of the Mo$_6$S$_2$I$_8$ nanowires in so-called “outside in” growth mode. The evolution of the transformation is proposed in a following way. Firstly, a kind of a MoS$_2$ envelope develops by a decomposition of the topmost layers of a Mo$_6$S$_2$I$_8$ nanowire and sulphurization of molybdenum. This protective overlayer influences the further decomposition of the precursor crystal by two ways: i) it prevents an easy escape of iodine and subsequent fragmentation of the nanowire, ii) it controls the entering of H$_2$S gas needed for the sulphurization of molybdenum in the nanowire inside. Later, a diffusion of iodine and/or iodine-molybdenum molecules takes place until all molybdenum reacts with H$_2$S gas and chemically liberated iodine can escape forming a lack of material and creation of gaps among cylinders. These nanotubes were lithium intercalated in a solution of butyl lithium in hexane at room temperature. The exfoliation occurs by immersing intercalated sample into water. Results of scanning electron microscopy, transmission electron microscopy and scanning tunnelling microscopy will be presented.

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Growth and Low Dimensional Properties of Novel Transition Metal Trichalcogenide Nanostructures

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One-dimensional (1D) inorganic nanostructures such as nanowires, nanorods and nanobelts, are of interest because they can display unique electric, optical, chemical and thermal properties. [1] In our continuing work on early transition metal chalcogenide nanomaterials, [2,3] we have recently focused on varying the symmetry and complexity of nanostructured materials in the early transition metal chalcogenide systems and are currently focusing our investigations on group IV and V trichalcogenides, MQ₃ (Q = S, Se, Te). Here we present results of investigations into nanostructured materials in the Ta-S and Ta-Se systems including the growth of rings, ribbons and möbius strips of TaSe₃.

Using chemical vapour transport (CVT) methods we have investigated the unusual effects on structure that can occur when the stoichiometry of the initial reactants and synthesis temperature are varied. When a balance between these two factors is successfully found, structures other than wires and tubes can be formed (depending on the system) and these factors can be potentially finely controlled and exploited. Furthermore, as a next step, it is anticipated that by using microfabricated (patterned) metallic films, it should be possible to grow these structures in prescribed patterns. Here we discuss the results of our initial studies of synthesis routes, growth, crystal structure, morphology and electronic structure and how these various facets of MQ₃ nanomaterials chemistry might be interrelated.

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Sb$_2$S$_3$ as a Light Absorber in Nanoporous Solar Cells

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Nanoporous solar cells are based on a nanoporous oxide substrate to remove electrons (usually TiO$_2$ or ZnO) on which is deposited a very thin (from molecular thickness to several tens of nm) light absorber, and then infiltrated with a hole conductor (e.g., an electrolyte or CuSCN). If the overall cell is solid state with a semiconductor absorber, the cells are commonly called Extremely Thin Absorber (or ETA) cells.

We describe ETA cells using Sb$_2$S$_3$ as the light absorber deposited on nanoporous TiO$_2$.

The cells are fabricated by solution processing. Sb$_2$S$_3$ is an uncommon constituent of solar cells, but, as we show, has several promising features. As the absorber in ETA cells, very high external photon-to-electron quantum efficiencies (over 80%) and solar conversion efficiencies over 3% have been obtained.

We describe the fabrication and properties of these cells, emphasizing some of the interface engineering issues and how they affect the cell properties.

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Progress in Synthesis and Characterization of IF Structures

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The quest for newly synthesized IF materials provides new structures and new materials continuously. The combination of high resolution electron microscopy (HRTEM) with synthetic techniques, modeling and theoretical calculations, raises new intriguing questions regarding the structure and function relationship of these structures. Moreover, in some cases the understanding of the structure may be the main approach to gain insights regarding the reaction path, for example.

In this talk I will review and summarize the main advancements and progress achieved in the last year by the collaborative work of three groups and I will mention a few of the future directions we intend to pursue.