

First symposium on
Transition Metal Chalcogenide Nanostructures
(TMCN07)

Rathen, Germany
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Abstract Book

Organizers:

Gotthard Seifert (Technical University Dresden, Germany)
Reshef Tenne (Weizmann Institute of Science, Israel)
David Tománek (Michigan State University, USA)

Time	Sunday March 18	Monday March 19	Tuesday March 20	Wednesday March 21
8:00-9:00		Breakfast	Breakfast	Breakfast
9:00-9:20		Opening	M. Remskar (<i>Jozef-Stefan Institut, Ljubljana</i>) The W ₅ O ₁₄ nanowires as precursors for WS ₂ nanotubes and fullerenes	Departure
9:20-9:40		R. Tenne (<i>Weizmann Institute</i>) Inorganic nanotubes and fullerene-like structures (IF): a progress report	T. Heine (<i>TU Dresden</i>) Mechanical Stability of MoS ₂ nanotubes	
9:40-10:00		A. Enyashin (<i>TU Dresden</i>) Structure and Stability of Molybdenum Sulfide Fullerenes	E. Dobardzic (<i>University of Belgrade</i>) Vibrations of MS ₂ (M=Mo, W) nanotubes	
10:00-10:30		Coffee	Coffee	
10:30-10:50		S. Gemming (<i>FZ Dresden</i>) From Clusters to wires – DFT investigations of molybdenum sulfide nanostructures	J.V.Lauritsen (<i>University of Aarhus</i>) Size-dependent structure of MoS ₂ nanocrystals observed with atom-resolved Scanning Tunneling Microscopy	
10:50-11:10		Teng Yang (<i>Michigan State University</i>) Improving upon carbon nanotubes with molybdenum chalcogenide nanowires	W. Tremel (<i>Universität Mainz</i>) Layered Chalcogenide Nanoparticles and Nanotubes	
11:10-11:30		I Vilfan (<i>Jozef-Stefan Institut, Ljubljana</i>) Structure and stability of MoSI	T. Fischer (<i>Universität Konstanz</i>) - to be announced -	

			nanowires: a DFT study		
12:00-14:00		Lunch			Lunch
14:00-15:00		<i>Discussion</i>			
15:00-15:20		C. Gademayer (Jozef-Stefan Institut, Ljubljana)	Equilibrium and non-equilibrium optical properties of MoSI nanowires	S.K. Klitgaard (TU Topsoe)	Template-directed synthesis of chalcogenide nanostructures
15:20-15:40		A. Zimina (BESSY m.b.H., Berlin)	Electronic structure of Mo-S-I nanostructures studied by soft X-ray spectroscopy	I. Popov (TU Dresden)	Structural and Electronic Properties of Mo ₆ S ₈ Clusters Deposited on a Au(111) Surface
15:40-16:00		J. Musfield (University of Tennessee)	Bulk vs. Nanoscale WS ₂ : Quantum Size Effects and Solid State Lubrication	J. Frenzel (MPI CPFS Dresden)	Structural, electronic and optical properties of Cadmium Sulfide Nanoparticles
16:00-16:30		Coffee			
16:30-17:30		<i>Discussion</i>			
17:30-17:50	Arrival	I. Milosevic (University of Belgrade)	Polarized optical absorption of transition metal disulfide nanotubes	M. White (Brookhaven)	Characterization and Reactivity of Size-Selected Metal Sulfide Clusters
19:00	Dinner	Dinner			Dinner

Polarized optical absorption of transition metal disulfide nanotubes

Ivanka Milosevic¹, E. Dobardzic¹, B. Nikolic¹, M. Damnjanovic¹, I. Popov², G. Seifert²

¹ University of Belgrade

² TU Dresden

Contact e-mail: *ivag@afrodita.rcub.bg.ac.yu*

Symmetry based calculations of the polarized optical conductivity of single-wall MS_2 ($M=Mo,W$) nanotubes are performed. Optical conductivity tensor for the individual tubes is numerically evaluated, using line group symmetry implemented POLSym code and DFTB-calculated Slater type orbital functions and Hamiltonian/overlap matrix elements, as input data. This minimal, full symmetry implementing algorithm enables calculations of the optical response functions very efficiently and to consider the highly chiral nanotubes (which have huge number of atoms within a unit cell) as well. The absorption spectra dependence on the diameter and chiral angle of the nanotubes is investigated. The results obtained are related to the measured spectra.

Characterization and Reactivity of Size-Selected Metal Sulfide Clusters

Michael G. White¹, James L. Lightstone², Melissa J. Patterson², Ping Liu³, John C. Lofaro²

¹ Brookhaven national Laboratory

² SUNY Stony Brook

³ Brookhaven National Laboratory

Contact e-mail: *mgwhite@bnl.gov*

The layered (S-M-S) structure of the bulk metal sulfides leads to unusual structures at the nanoscale (disks, fullerenes, tube) that exhibit a size-dependent band gap and/or unique catalytic properties. Indeed, MoS₂ is widely used as a commercial catalyst for hydrogenation, hydrodesulfurization, and hydrodenitrogenation, where it is dispersed as nanoparticles (10-30 Å) on a high surface area support. It is generally accepted that the active sites for reaction are associated with Mo atoms (with Ni/Co promoter atoms) located at defects or edges of the nanoparticle, however, many questions remain about the inter-relationship between nanocluster size, structure (atomic and electronic) and metal-sulfur composition, and how these physical properties influence catalytic activity.

In this work, we are using mass (size) selected cluster ion beams to explore the size dependent reactivity of small nanoclusters of the early transition metal sulfides (Mo, W). Specifically, we use reactive sputtering in a magnetron source to generate gas-phase cluster cations which are then mass-analyzed to yield a beam of clusters with a precisely defined mass (size) and metal-sulfur composition. The gas-phase chemistry can be studied by passing the clusters through a high-pressure collision cell and downstream product detection. Alternatively, the mass-selected clusters can be deposited at low kinetic energies (“soft landing”) onto a solid support for preparing model nanocatalysts whose properties can be studied by conventional surface science techniques.

To date, we have explored the structure and stability of several prominent M_xS_y⁺ and W_xS_y⁺ cluster species ($x/y = 2/6, 3/7, 4/6, 5/7, 6/8, 7/10, 8/12$). Structural information is derived from comparisons between the observed and calculated relative stability of the adducts formed between the M_xS_y⁺ clusters and CO (or NH₃). Of particular interest is the M₄S₆⁺ “magic number” cluster which is calculated (DFT) to be a compact cluster with the four metal atoms arranged in an internal tetrahedron surrounded by bridging S-atoms (near T_d symmetry). We are also investigating the structure and reactivity of M_xS_y clusters ($x/y = 3/7; 4/6; 5/7; 6/8; 7/10$) deposited on a Au(111) surface. The Au(111) surface is often used as a support for such studies due to its relative inertness and its characteristic herringbone surface structure which serves as a template for nanocluster nucleation. Preliminary results show that the clusters can be deposited intact on the Au surface with adsorbate binding energies which depend on cluster size and the presence of the Au substrate.

Structure and stability of Mo-S-I nanowires: a DFT study

Igor Vilfan

J. Stefan Institute

Contact e-mail: *igor.vilfan@ijs.si*

The possible structure and stability of different $\text{Mo}_6\text{S}_x\text{I}_{9-x}$ ($x = 0..9$) stoichiometries are investigated with the density-functional theory (DFT) methods as implemented in the WIEN2k package. Common to all these nanowires is the skeletal structure, composed of Mo octahedra, each dressed with 6 anions and linked into one-dimensional chains with three bridging anions.

We will look into more detail of $\text{Mo}_6\text{S}_3\text{I}_6$, which has been synthesized recently and whose anion arrangement and crystal ordering are still controversial. Whereas the first experiments suggested the chain ordering according to the space group $P6_3$ [1], more recent experiments and simulations suggest the very low-symmetry P-1 space group [2]. We come to a different conclusion, our DFT simulations suggest three Mo-S-I chains per hexagonal unit cell, shifted along the hexagonal c axis by 0, 1/3 and 2/3, respectively. We also find a tendency for S atoms to bind to the dressing anion sites. Similarity in the energies of nanowires with the same stoichiometry and different anion occupancies strongly indicate the possibility of anion occupational disorder.

In general, our DFT simulations show a strong correlation between the stability of Mo-S-I nanowires and the Mo oxidation state, weak coupling between individual molecular chains and consequently to quasi-one dimensional physical properties of these nanowires.

References

- [1] A. Meden et al, Nanotechnology **16** , 1578 (2005).
- [2] V. Nicolosi et al, submitted.

Vibrations of MS_2 (M=Mo, W) nanotubes

Edib Dobardzic¹, Ivanka Milosevic², Borivoje Dakic², Milan Damnjanovic²

¹ Faculty of Physics, University of Belgrade

² Faculty of Physics, Belgrade, Serbia

Contact e-mail: *edib_dobardzic@ff.bg.ac.yu*

We have calculated phonon energies of all the single-wall MS_2 nanotubes with diameter range 1-20 nm, using full symmetry implemented valence-force-field model. In particular, we extracted infrared and Raman active modes in order to clarify possible application of these methods in the experimental sample characterization. A prescription for experimental distinction of zig-zag, armchair and chiral tubes, based on their different symmetry and resulting selection rules, is proposed. Furthermore, we noticed that displacements significantly depend on the chiral angle only for two modes in MoS_2 nanotubes, namely twisting in-phase (rigid layer) and breathing out-of-phase, and none of WS_2 modes. Also, we found that heat capacity of the nanotubes and corresponding layer are similar.

Structural, electronic and optical properties of cadmium sulfide nanoparticles

Johannes Frenzel¹, Jan-Ole Joswig², Gotthard Seifert²

¹ MPI CPFS

² Physikalische Chemie, TU-Dresden

Contact e-mail: *frenzel@cpfs.mpg.de*

Focussing on the influence of the surfactants (unsaturated, partly saturated, completely saturated) on the structural, electronic and optical properties of cadmium sulfide nanoparticles calculations on structures with up to 2000 atoms have been performed employing density-functional and linear-response theory. Furthermore, we studied the aspects of different stoichiometries, underlying crystal structures (zinc-blende, wurtzite, rock-salt), particle shapes (spherical, cuboctahedral, tetrahedral), and the organization of single clusters forming macroscopic crystals.

We show, that through the saturation of the surface valences the atomic structure is stabilized (reducing surface reconstruction and ionicity). The electronic structure changes as well. In particular, the surface saturation affects the states closest to the Fermi level, and, thus, the optical properties. For the saturated particles, the quantum-confinement effect in the lowest excitation is observable as the excitation energy decreases towards the bulk band gap with increasing particle size. We find strong excitonic onset excitations. Dangling bonds at unsaturated surface atoms introduce trapped surface states which lie below the lowest excitations of the completely saturated particles. Zinc-blende- and wurtzite-derived particles show very similar spectra, whereas the spectra of rock-salt-derived particles are rather featureless. Particle shapes that confine the orbital wavefunctions strongly (tetrahedron) give rise to less pronounced, featureless spectra with lower oscillator strengths. Finally, we find a very good agreement of our data to experimentally available spectra and excitation energies.

Template-directed synthesis of chalcogenide nanostructures

Søren K Klitgaard¹, Kresten Egeblad¹, Michael Brorson², Thomas W Hansen²,
Claus H Christensen¹

¹ CSG, Technical University of Denmark

² Haldor Topsoe A/S

Contact e-mail: *skk@kemi.dtu.dk*

One of the many reasons that nano has had huge impact in the scientific community is the fact that many materials change properties upon going from the bulk state to the nanosized level, thereby opening up a whole new world of interesting physical and chemical properties. Changes in the nanostructures, like altering the diameter of nanotubes, will also lead to changes in the properties of nanotubes materials. By using templates in the synthesis of nanostructures it is possible to structurally direct the synthesis into a desired nanostructure. The templates can either be an inner type template, e.g. nanotubes or rods, or an outer type template having internal pores, e.g. zeolites or anodic aluminum oxide.

As being part of a newly started research project we present some ideas and visions on how to use structured templates in the synthesis of nanostructured material, mostly nanotubes, in order to study the different properties of these materials, especially the changes in electrical behaviors.

The main focus will be the use of carbon nanotubes with different diameter as an inner template for coating with metal sulfides and ordered structured materials like MCM-41, SBA-15 as structured outer templates. One of the advantages of using ordered structured materials as outer templates is the easy synthesis of these materials with different pore size.

The formation of nanostructured materials using templates often leads to higher selectivity in the formation of the desired materials. The application of templates in the synthesis of nanostructures may be the key to synthesizing new types of nanostructured materials from large numbers of well known layered structured materials.

Improving upon carbon nanotubes with molybdenum chalcogenide nanowires

Teng Yang¹, Igor Popov², Savas Berber¹, Gotthard Seifert², David Tomanek¹

¹ Michigan State University

² Physikalische Chemie, TU Dresden

Contact e-mail: yang@pa.msu.edu

We present the first *ab initio* study of a new nanowire with the composition $\text{Mo}_6\text{S}_4\text{I}_2$, which may solve some of the problems typically associated with carbon nanotubes (in particular strong conductivity dependence on chiral index, difficult dispersion, not well-defined contacts). We study the stability, electronic structure, and quantum transport of $\text{Mo}_6\text{S}_{6-x}\text{I}_x$ nanowires, where substitutional iodine optimizes the stability and conductance, and find many of the nanowire properties comparable to metallic carbon nanotubes. We find $\text{Mo}_6\text{S}_{6-x}\text{I}_x$ nanowires to be conductive irrespective of their structure, more easily separable than carbon nanotubes, and capable of forming ideal contacts to Au leads through thio-groups, which makes them especially attractive for experimental realization.

Structural and Electronic Properties of Mo_6S_8 Clusters Deposited on a Au(111) Surface

Igor V. Popov

Physikalische Chemie, TU Dresden

Contact e-mail: *Igor.Popov@chemie.tu-dresden.de*

The stability and the change of the structural and electronic properties of the molybdenum sulfide cluster Mo_6S_8 upon adsorption on the Au(111) surface are investigated by density-functional band-structure calculations with pseudopotentials and a plane wave basis set. The nearly cubic cluster preferably adsorbs via a face and maintains its structural integrity. It experiences a strong, mostly non-ionic attraction to the surface at several quasi-isoenergetic adsorption positions. The analysis of the electronic structure reveals a negligible electron transfer and S-Au hybridized states, which indicate that the cluster-surface interaction is dominated by S-Au bonds, with minor contributions from the Mo atom in the surface vicinity. All results indicate that Mo_6S_8 clusters on the Au(111) surface can undergo a template-mediated self-assembly to an ordered inorganic monolayer, which is still redox active and may be employed as surface-active agent in the integration of noble metal and ionic or biological components within nano-devices.

Equilibrium and non-equilibrium optical properties of MoSI nanowires

Christoph Gadermaier¹, Primoz Kusar¹, Damjan Vengust¹, Leonardo Degiorgi²,
Dragan Mihailovic¹

¹ Department of Complex Matter, Jozef-Stefan Institut, Ljubljana, Slovenia

² Laboratory for Solid State Physics, ETH Zürich, Switzerland

Contact e-mail: *christoph.gadermaier@ijs.si*

MoSI nanowires are the one-dimensional systems with the weakest known interaction with their neighbours. Therefore they are expected to show most clearly the effects of one-dimensionality. We studied equilibrium and non-equilibrium optical properties via optical reflectivity and absorbance as well as femtosecond pump-probe spectra of oriented MoSI nanowire thin films.

Absorption of light polarised parallel to the axis of orientation shows a series of resonances that are absent for perpendicular polarisation. The pattern of these resonances is in excellent agreement with the calculations. The sharp Van Hove features expected from the highly one-dimensional character of the material and the narrow valence and conduction bands of predominantly Mo-d and S-p character are not observed, partly because of the large density of electron sub-bands and partly because of electron energy damping.

Femtosecond studies presented will be discussed in terms of electronic structure, one-dimensional relaxation behaviour and propagation of impulsive mechanical strain.

Structure and Stability of Molybdenum Sulfide Fullerenes

Andrey N Enyashin, Gotthard Seifert

Physical Chemistry, Technical University Dresden

Contact e-mail: *enyashin@ihim.uran.ru*

The perspective applications of the inorganic hollow nanoparticles as elements of nanodevices and lubricants require their profound theoretical investigations.

In this work the structure models of the molybdenum sulfide fullerenes (nanooctahedra) both stoichiometric and nonstoichiometric composition were proposed. Using Density Functional Tight-Binding method (DFTB) for the first time was shown a high instability of the “ideal“ MoS₂ singlewalled nanooctahedra with sizes at least less than 1700 atoms. The most stable skeletons of fullerenes with nonstoichiometric composition at these sizes were found. Based on the DFTB estimations a model of stability for MoS₂ nanoforms (nanoplatelets, nanooctahedra and spherical nanoparticles) was developed. We would expect a stability of the MoS₂ manylayered fullerenes composed with more than 12000 atoms. Nanooctahedral fullerenes represent a window of stability between nanoplatelets and spherical nanoparticles.

In spite of bulk or nanotubular MoS₂ allotropes for all molybdenum sulfide nanoparticles a metallic-like character of electronic states is predicted.

Layered Chalcogenide Nanoparticles and Nanotubes

Wolfgang Tremel, Aswani Yella, Muhammad Nawaz Tahir, Helen Annal Therese,
Nicole Zink, Ute Kolb, Florian Banhart

Universität Mainz

Contact e-mail: tremel@uni-mainz.de

The synthesis of nanostructures from layered materials such as onion-like particles and nanotubes was first achieved in the carbon system. Tenne and co-workers opened up the pathway to a new class of compounds, layered transition metal chalcogenides MQ₂ (M = transition metal, Q = S, Se, Te) forming similar morphologies, and dubbed them inorganic fullerene-like materials (IF). Various synthesis techniques for these IFs have been established so far, among them oxide to sulfide conversion, transport reactions, laser ablation, arc discharge, template methods, microwave synthesis and chemical vapor deposition (CVD).

We report a mechanistic study of the synthesis of MQ₂ (M = Mo, W, Re) IF nanoparticles by means of a high temperature MOCVD process starting from the corresponding carbonyls and elemental sulfur. The reaction can also be carried out in two steps, where a reaction intermediate, amorphous MQ₂ nanoparticles that are formed through the high temperature reaction of the metal and sulfur, are isolated and converted in a separate annealing step to onion-type MQ₂ nanoparticles. Based on a study of the temperature dependence of the reaction a set of conditions could be derived where onion-like structures were formed in a one-step reaction. IF structures obtained in the single-step process were filled, whereas the particles obtained by the two-step procedure were systematically hollow. A model could be devised to rationalize the different outcome of the reactions. The MOCVD approach therefore allows a selective synthesis of open and filled fullerene-like chalcogenide nanoparticles.

In order to understand to solid state transformations associated with the fullerene formation in situ heating transmission electron microscopy (TEM) studies were conducted on MoS₂, WS₂ and ReS₂ nanoparticles obtained from MOCVD. The general behavior of all materials is similar: round, amorphous precursor particles in the pristine sample transform to hollow, onion-like particles upon annealing. A second type of particles with straight layers does exhibit only minor changes. A significant difference between both compounds could be demonstrated in their crystallization behavior. The results of the in situ heating experiments are compared to those obtained from an ex situ annealing process under Ar.

Chalcogenide nanotubes and particles obtained from the above processes represent attractive building blocks for the hierarchical assembly of functional nanoscale devices that eventually could overcome fundamental and economic limitations of conventional lithography-based fabrication. The sandwich-type structure of the metal dichalcogenide particles, however, requires a covalent functionalization strategy different from that employed for oxide or carbon nanoparticles. using chelating ligands.

The W5O14 nanowires as precursors for WS2 nanotubes and fullerenes

Maja Remskar, Marko Virsek, Adolf Jesih

Jozef Stefan Institute

Contact e-mail: *maja.remskar@ijs.si*

The Magneli phases are homologous series of quite stoichiometric phases of transition metal suboxides with unusual composition. Recently, research of nanomaterials with their size dependent and low-dimensional physical and chemical properties recalled the scientific attention to tungsten sub-oxides, which show high aspect ratio and promising physical properties in nanodimensions. In 1978, the W5O14 phase was reported for the first time by I.J. McColm et al. (J. Solid State Chem. 23, 33 (1978)). The phase consisted of purple-blue fibres appeared after relatively long heating times- one week, at 1100°C. In meantime, this particular sub-oxide was declared as the compound, which may hardly exist, maybe as a possible oxygen-deficient phase occurred during laser deposition of polycrystalline WO3.

We'll report on a novel type of synthesis, where mostly pure quasi one-dimensional W5O14 phase occurs from vapour phase at relatively low temperature of 736°C. Scanning electron microscopy and transmission electron diffraction data are correlated with details of crystal growth revealing the possible mechanism of the formation of this rarely synthesized phase. Scanning tunnelling spectroscopy and direct transport measurements reveal metallic conductance of the W5O14 nanowires, that enables to rank them among promising family of molecular wires.

The W5O14 nanowires have been used as precursors for synthesis the WS2 nanotubes by sulphurization in the mixture of 1% H2, 1% H2S in argon. The produced nanotubes are mainly closed and of very regular structure. Their diameter is much smaller than the wideness of precursor nanowires revealing exfoliation of the precursors, while the length up to several hundreds microns frequently matches the length of the W5O14 nanowires. Beside nanotubes, the WS2 fullerenes grow simultaneously. This is the first evidence that the WS2 fullerenes can grow by diffusion process without spherical precursors. The details of the transformation process will be presented revealing the importance of hexagonal 2Hb stacking.

Electronic structure of Mo-S-I nanostructures studied by soft X-ray spectroscopy.

Anna Zimina¹, Stefan Eisebitt², Wolfgang Eberhardt², Dragan Mihailovic³, Igor Vilfan³,
Daniel Vrbanic³

¹ BESSY m.b.H.

² BESSY m. b. H.

³ Jozef Stefan Institut

Contact e-mail: zimina@bessy.de

The first description of the synthesis of single-wall MoS₂-I_x nanotubes (SWNTs) in the Jozef Stefan Institute (Ljubljana, Slovenia) was reported in 2001 [1]. They appeared to be monodisperse, of less than one nanometer diameter and self-organized into bundles. Our results on the electronic structure of those NTs studied by soft X-ray spectroscopy were reported in [2]. A follow-up study designed to find other one-dimensional transition-metal chalcogenide-based nanowires and nanotubes resulted in the discovery of new nanowire materials with the formulas Mo₆S₃I₆ [3, 4] and Mo₆S_{4.5}I_{4.5} [5]. Recent results on the electronic structure of Mo₆S_(9-x)I_x nanowires (x=6, 4.5) studied by soft X-ray absorption and emission spectroscopies are presented. To study how the electronic structure of the tubes changes with the geometry the atomic selectivity of the method was utilized by observing an inelastic scattering at the S 2p excitation threshold. The experimental data are compared to the DFT electronic structure calculations.

[1] M. Remskar et al. *Science*, 292, 479 (2001)

[2] A. Zimina et. al. *Nano Letters*. 4, 1749-1753 (2004)

[3] V. Vrbanic et. al. *Nanotechnology*, 15(5), 635 (2004)

[4] A. Meden et. al. *Nanotechnology*, 16, 1578 (2005)

[5] V. Nicolosi et. al *Chem. Phys. Lett.*, 401, 13 (2005)

Size-dependent structure of MoS₂ nanocrystals observed with atom-resolved Scanning Tunneling Microscopy

Jeppe V Lauritsen¹, Jakob Kibsgaard¹, Henrik Topsøe², Bjerne S Clausen²,
Flemming Besenbacher¹

¹ University of Aarhus

² Haldor Topsøe A/S

Contact e-mail: jvang@phys.au.dk

We have used Scanning Tunneling Microscopy (STM) to investigate the atomic-scale structure of 1-3 nm wide single-layered MoS₂ nanoclusters supported on a gold substrate. Our main interest has been to investigate the structure of MoS₂ in relation to its catalytic properties as supported nanoclusters in the important hydrotreating catalysts are used for upgrading and cleaning impurities from crude oil. It has been established that only the edges of single-layer MoS₂ are reactive, but the exact configuration of the active sites is still a matter of considerable debate, which is largely due to lack of detailed insight at the atomic level. The STM images reveal that the equilibrium shape of MoS₂ nanocrystals synthesized under sulfiding conditions is a triangle independent of its size. Atom-resolved STM images of individual clusters provide information of the important cluster edges, and in interplay with density functional theory we are able to identify the cluster edge configurations. Larger clusters seem to be terminated by only one type of low-index edge, the MoS₂ (10-10) edge (Mo edge), with every Mo edge atom fully coordinated to S₂ dimers. In the STM images we find a pronounced brim structure adjacent to the edges on top of these clusters, which is associated with a one-dimensional metallic edge states. These “metallic” brims are shown to contain unusual sites that may play an important catalytic role, since they are shown in STM experiments to have the capability to adsorb thiophene (C₄H₄S) and facilitate a hydrogenation reaction and C-S cleavage. A further analysis of the MoS₂ triangles as a function of size, however, reveals that small clusters with a certain size are more stable than others, and atom-resolved images show that the most stable small clusters may be terminated by new edge configurations. Specifically, we find that clusters containing less than 21 Mo atoms prefer to be terminated by (-1010) S edges with varying sulfur coverage, and the general trend is that clusters with a total S : Mo ratio above approximately 3.5 : 1 seem to be energetically disfavored, as evidenced by their absence in the equilibrium ensemble of clusters. We show that there is a direct link between the structural transitions observed in the STM experiments and the tendency to reduce the sulfur content in the clusters below this limit. The novel findings suggest that good size control during the synthesis of MoS₂ nanostructures may be used for the production of chemically or optically active MoS₂ nanomaterials with superior performance.

Inorganic nanotubes and fullerene-like structures (IF): a progress report

Reshef Tenne

Weizmann Institute

Contact e-mail: *reshef.tenne@weizmann.ac.il*

In this presentation a progress report, focused mainly on the results obtained in our lab will be presented. While the synthesis and study of IF materials from layered metal dichalcogenides, like WS₂ and MoS₂ remain a major challenge, some progress with the synthesis of IF structures from other compounds, like metal oxides and metal halides have been realized. The synthesis of some new IF materials, like Cs₂O, NiBr₂ and others will be described.

The study of the mechanical properties of individual WS₂ nanotubes will be discussed in some detail. The agreement between theory and experiment suggests that the nanotubes are of high crystalline order and their mechanical properties are predictable.

The study of MoS₂ nanooctahedra 3-6 nm in size, which can be considered to be the true inorganic fullerenes of these and many other layered structures, will be discussed. The agreement between the calculated and experimentally observed structures indicate that the nanooctahedra are indeed the stable structures in this size range, beyond this size the quasi-spherical nested MoS₂ structures become stable.

Some new potential applications for these and related materials will be discussed in the fields of friction reduction of various objects; catalysis; rechargeable batteries, coatings, etc. will be discussed as well. To capitalize on these opportunities, a production facility for up to 100 kg/day of IF-WS₂ has started operating recently.

Mechanical stability of MoS₂ nanotubes

Thomas Heine¹, Andrey N. Enyashin², Milen St. Stefanov-Dobrev³, Gotthard Seifert²

¹ TU Dresden

² Physikalische Chemie, TU Dresden

³ ENSC Montpellier, France

Contact e-mail: *thomas.heine@chemie.tu-dresden.de*

MoS₂ nanotubes have interesting mechanical properties, in particular a high stability under axial tension. On the other hand, adding MoS₂ multi-layer fullerenes to base grease results in new lubricants with very low friction coefficients. Recent computer simulations show that the deformation of MoS₂ tubes under radial compression follows a different mechanism, and implies a different explanation of the excellent lubricating properties of the material.

Bulk vs. Nanoscale WS₂: Quantum Size Effects and Solid State Lubrication

Janice L. Musfeldt¹, S. Brown¹, I. Mihut², J. B. Betts², A. Migliori², A. Zak³, R. Tenne⁴

¹ University of Tennessee

² Los Alamos National Laboratory

³ NanoMaterials Ltd.

⁴ Weizmann Institute of Science

Contact e-mail: *musfeldt@utk.edu*

Metal dichalcogenide nanostructures have recently attracted attention due to their unique closed-cage structures, hierarchy of length scales, and outstanding solid state lubrication behavior. To understand the finite size effects and tribological properties in these nanoscale materials, we measured the low temperature specific heat of layered and nanoparticle WS₂. Below 9 K, the specific heat of the nanoparticles deviates from that of the bulk. Further, the thermal response of the nested nanoparticles deviates from the usual T³ dependence below 4 K because of both finite size effects and inter-particle-motion entropy. This separation of nanoscale effects from T³ dependence can be modeled by assuming that the phonon density of states is flexible, changing with size and shape of the nanoparticle. We also invoke relationships between the low temperature T³ phonon term, Young's modulus, and friction coefficient to assess the difference in the tribological properties. Based on this analysis, we conclude that the improved lubrication properties of the nanoparticles are extrinsic in origin.

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