

## Structural properties of chalcogenides nanostructures

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Following the discovery of carbon fullerenes and nanotubes (NTs), nanostructured materials and their synthesis have attracted tremendous attention due to their superior mechanical properties, their unique electronic behavior, and their high potential in making technologically advanced nanodevices. Among different classes, layered metal chalcogenides nanostructures are of interest for a variety of applications ranging from nanoelectronics or as source materials for energy applications, nanotribology and in heterogeneous catalysis. These nanoparticles are metastable phases. Therefore, equilibrium methods are necessary to prevent the formation of the thermodynamically stable bulk phase. On the other hand, high energies are needed to “knit” together the folded layers. Several physical techniques such as laser ablation and arch discharge are used for the synthesis of these inorganic NTs and fullerene-like particles. Apart from these high-energy techniques other processes such as oxide-to-sulfide conversion, hydrothermal, solvothermal, or wet chemical synthesis were found to be useful for the synthesis of these particles.

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**Keywords:** Chalcogenide; Nanostructure; Mechanical.

### 1. INTRODUCTION

Following the discovery of carbon nanotubes (NTs) in 1991 [1], nanostructured materials and their syntheses have attracted tremendous attention due to their superior mechanical properties, their unique electronic behavior, and their high potential in making technologically advanced nanodevices. Along with carbon NTs, many non-carbon nanostructures have been synthesized during the past few years. Owing to their unusual geometry and promising physical properties, the study of inorganic layered chalcogenide nanostructures has become one of the key topics in nanoscale research since the fi st

report on WS<sub>2</sub> NTs and fullerenes by Tenne et al. in 1992 [2]. Various approaches to other inorganic NTs, such as NiCl<sub>2</sub> [3], VS<sub>2</sub> [4], TiS<sub>2</sub> [5], and InS [6], have also been reported, which implies that many layer compounds may form fullerenes or NTs under favorable conditions. Chalcogenide nanostructures are of interest for a variety of applications ranging from nanotribology, nanoelectronics, or battery materials to the active use in heterogeneous catalysis. Similar as their carbon congeners, chalcogenide nanoparticles are not equilibrium but high-temperature and low-pressure phases that are obtained by quenching “hot” gas-phase species. However, the synthesis of chalcogenide NTs and fullerenes (inorganic fullerenes, IFs) is, in contrast to carbon, difficult owing to their wall thickness of three atom layers; considerable strain energy is required to achieve surface curvature [7]. Layered chalcogenides (MQ<sub>2</sub>, M=Mo, W, Re, or Sn, Q = S, Se) are triple-layer structures in which one metal layer is sandwiched between two chalcogenide layers [8]. In contrast to carbon NTs, no catalyst aids in their formation. The formation of curved MQ<sub>2</sub> morphologies commonly involves a considerable number of lattice defects and dislocations [9]. Since the first observation of single NTs [2], significant progress has been made, and today gram quantities of some metal chalcogenide NTs can be obtained in pure form.

During the past few years, various strategies have been developed to prepare nanostructured metal sulfides and selenides through different growth mechanisms. A characteristic feature of all closed-shell structures is that high reaction temperatures (>800°C) or large activation energies are needed to overcome the activation barrier associated with the bending of the otherwise flat two-dimensional (2D) layers [10]. Although various synthetic approaches to chalcogenide nanoparticles have been established so far, their growth mechanism is still subject to discussion. Tenne and co-workers were the first to show that fullerene-type nanoparticles or nanopolyhedra and NTs represent an integral part of the phase diagram of MoS<sub>2</sub> and WS<sub>2</sub> [11]. In the following decade, a variety of methods including arc discharge [12,13], sulfurization/selenization of metal oxides [14–24], chlorides [25,26], carbonyls [27], decomposition of ammonium thiometalates [28–31], chemical vapor transport [32–33], laser ablation [34–37], microwave plasma [38,39], atmospheric pressure chemical vapor deposition (APCVD) [40], or spray pyrolysis [41] were utilized for the synthesis of IF- or NT-like structures of MQ<sub>2</sub> materials.

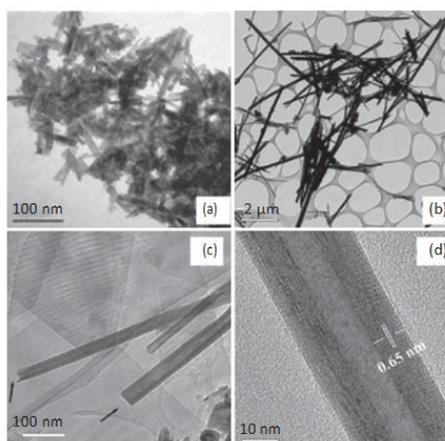
Nanotechnology aims at manipulating atoms, molecules, and nano-size particles in a precise and controlled manner in order to build materials with a fundamentally new organization and novel properties. The embryonic stage of nanotechnology is atomic assembly whereas the mature form of nanotechnology will be molecular assembly to make nano-building blocks for the design of nanocomposites or self-organizing nanodevices. In order to benefit from the outstanding properties of NTs, their functionalization is essential, as any application in materials and devices is hindered by difficulties in processing and manipulation. Only the attachment of appropriate chemical functionalities on the NT surface allows a tailoring of their properties for the respective application. As an example, the enhancement of the NT solubility is one major task since most pristine NTs are insoluble in both water and organic solvents. Thus, the improvement of the solubility by chemical functionalization is an important task for synthetic chemists and materials scientists. Tailoring of the surface chemical bonds might as well lead to an optimized interaction of the NTs with solvent molecules, polymer matrices, or biomolecules. Therefore, the nanoengineering of particle surfaces is a key for the design and tailored construction of innovative nanomaterials [42]. Having control of the inorganic nanoparticle surfaces allows one to tailor the particle size [43] and solubility [44]. Moreover, the surface characteristics of nanomaterials influence the broad range of properties and the performance of a large variety of devices. For instance, the charge transport process across the interface between a semiconductor metal oxide and an organic dye [45] or a biomolecule [46] forms the basis for improving the performance of many optoelectronic devices, photovoltaic cells [47], and light-emitting diodes (LEDs) [48]. Oligonucleotides can also be linked to surfaces of nanoparticles, which may become a new tool for gene therapy [49].

## 2. EXPERIMENTAL

During the past few years, various strategies have been developed to prepare nanostructured metal sulfides and selenides through different growth mechanisms. A characteristic feature of all closed-shell structures is that high reaction temperatures ( $>800^{\circ}\text{C}$ ) or large activation energies are needed to overcome the activation barrier associated with the bending of the otherwise flat 2D layers. Although various synthetic approaches to chalcogenide nanoparticles have been established so far, their growth mechanism is still subject to discussion. Tenne and co-workers were the first to show that fullerene-type nanoparticles or nanopolyhedra and NTs represent an integral part of the phase diagram of MoS<sub>2</sub> and WS<sub>2</sub> [2]. One of the methods already known from the synthesis of C<sub>60</sub> is laser ablation of a suitable target material. Soon after the synthesis of NiCl<sub>2</sub> NTs and fullerene-like particles by laser ablation, Parilla et al. yielded nano-octahedra of MoS<sub>2</sub> with the same method, which was later extended to MoSe<sub>2</sub>. Metal-filled and hollow IF-like particles of MoS<sub>2</sub> and WS<sub>2</sub> were obtained some years later by Sen et al. Recently, Schuffenhauer et al. obtained filled TaS<sub>2</sub> fullerene-like particles by laser ablation of TaS<sub>2</sub> under Ar and CS<sub>2</sub>, respectively. Hf<sub>2</sub>S-IFs could be synthesized via laser ablation in a liquid medium. Laser ablation in water resulted in hexagonal WS<sub>2</sub> nanoparticles. Faceted IFs consisting of SnS<sub>2</sub> and SnS were synthesized by Hong et al. The microwave-induced plasma method gives access to a large variety of compounds. By reacting M(CO)<sub>6</sub> with H<sub>2</sub>S or SeCl<sub>4</sub>, Vollath and Szabo obtained MQ<sub>2</sub> (M=Mo, W; Q= S, Se) nanoclusters, partly also in the form of fullerene-like particles. Furthermore, nanoclusters of SnS<sub>2</sub> and ZrS<sub>2</sub> were prepared with the same setup. Starting from WO<sub>3</sub> nanoparticles, ZrS<sub>3</sub> or HfS<sub>3</sub>, Brooks et al. obtained WS<sub>2</sub> and HfS<sub>2</sub>-IFs, and ZrS<sub>2</sub> NTs and nanorods, respectively, in microwave-induced plasmas of H<sub>2</sub>S and N<sub>2</sub>/H<sub>2</sub>.

## 3. RESULTS AND DISCUSSION

Among the number of methods used for the synthesis of layered chalcogenide NTs, the most successful is the reductive sulfidization of oxide nanoparticles using H<sub>2</sub>S. Initial studies were carried out on the conversion of tungsten oxide nanorods to NT-WS<sub>2</sub>. The tungsten oxide nanorods were synthesized using a sol-gel technique, and the as-synthesized nanorods were used for the conversion to the sulfide NTs. Hexagonal WO<sub>3</sub> nanorods of 5–50 nm in diameter and 150–250 nm in length were obtained using the sol-gel process. These WO<sub>3</sub> nanorods were highly suitable as a precursor for the synthesis of multi-walled NT-WS<sub>2</sub> by reduction with H<sub>2</sub>S at 840°C for 30 min. The length and the wall thickness of the WS<sub>2</sub> NTs could be altered by controlled reduction of the oxide precursor.

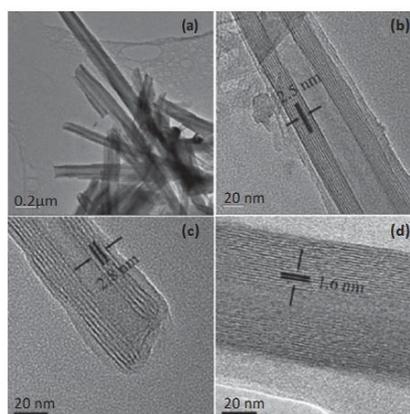


**Figure 1** TEM (a and b) and HRTEM (c and d) images of the oxide nanorods (a) and the product obtained after sulfidization of the oxide nanorods (b–d).

Figure 1 shows TEM and high-resolution transmission electron microscope (HRTEM) images of the oxide nanorods and the sulfide NTs WO<sub>x</sub> from the vapor state. A similar mechanism is plausible in the

present NT synthesis, where the reducing H<sub>2</sub>/N<sub>2</sub> gas was replaced by a pre-treatment of the oxide with Ar gas. A TEM analysis of the oxide rods after the pretreatment with Ar shows the formation of an intermediate tungsten oxide with many defects while the appearance of the rods was retained. This could be related to a higher surface activity of the oxide nanorods. The morphology of the starting compounds is intimately connected to the morphology of the final products. It is not only the spherical nanoparticles and nanorods that can be converted to the corresponding sulfide hollow structures, but also the oxide NTs with an amine template molecule intercalated between the layers can also be converted to the sulfide NTs by retaining their original tubular morphology.

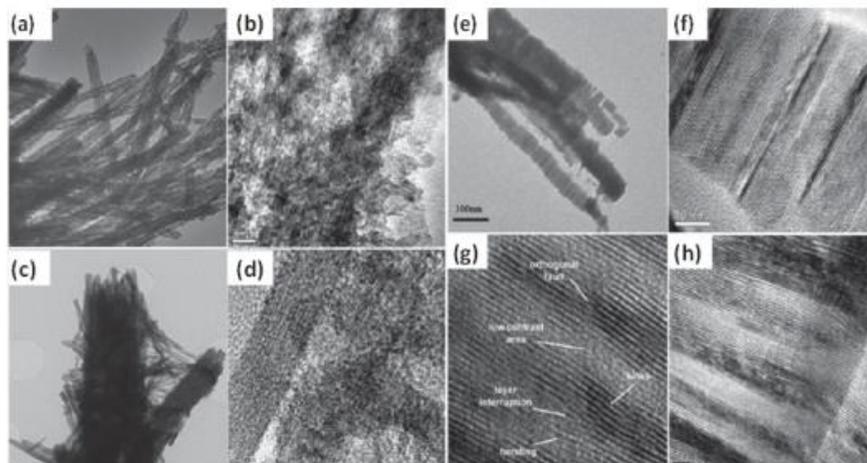
The amine-intercalated vanadium disulfide NTs are the first layered chalcogenide NTs in which the organic molecules are intercalated in between the layers. Figure 2 shows TEM and HRTEM images of a partially and a fully sulfidized VS<sub>2</sub> NT with lattice fringes corresponding to a layer separation of approximately 2.8 nm (partially sulfidized) and 1.6 nm (fully sulfidized). These values are significantly larger than the layer separations in bulk VS<sub>2</sub> (0.57 nm), resulting from the sulfidization. A mechanism for the growth of NTs from oxide whiskers and rods has been proposed previously by Tenne and co-workers. According to this mechanism, the growth of WS<sub>2</sub> layer starts by engulfing the WO<sub>x</sub> particle in the initial phase of the reaction with a mantle of WS<sub>2</sub>. During the course of the reaction, this embryonic WS<sub>2</sub> layer starts growing inward as well as slowly converting of the oxide, which is continuously growing on the other end of the particles by the condensation of As a step further, the oxide-to-sulfide conversion technique was employed for the synthesis of the doped inorganic NTs. The niobium oxide nanorods were synthesized by a sol-gel process. And the as obtained Nb<sub>2</sub>O<sub>5</sub> NWs were then coated with tungsten oxide by using a solvothermal approach. The coated oxide nanorods upon annealing leads to the diffusion of tungsten into the niobium lattice resulting in the formation of mixed oxide nanorods. The coated NWs were sulfidized in a reaction by heating the coated NWs in Ar gas to 850°C while passing a stream of a H<sub>2</sub>S for 30 min. Oxide-to-sulfide conversion takes place analogously to the way described for pure WS<sub>2</sub> NTs resulting in the formation of Nb-W-S composite nanostructures. The product contains stacked MS<sub>2</sub> platelets with diameters ranging from 40 to 60 nm, while the length of the stacks varies between 1 and 8 μm.



**Figure 2** TEM and HRTEM images of the product obtained after the sulfidization of vanadium oxide NTs. (a) Low-resolution overview TEM image of VO<sub>x</sub> NTs used as a starting material for the synthesis of NT-VS<sub>2</sub>. (b) HRTEM image of a single VO<sub>x</sub> NT with a layer separation of 2.5 nm. (c) HRTEM image of a single VS<sub>2</sub> NT obtained from NT-VO<sub>x</sub> intercalated with C16-amine with a layer separation of 2.8 nm and a flat cap, showing a partially crystalline or amorphous coating. (d) HRTEM of a NT-VS<sub>2</sub> obtained from NT-VO<sub>x</sub> intercalated with C12-amine, with a layer d-spacing of 1.6 nm.

HRTEM images show these structures to be very different from the conventional curved nanostructures typically observed for layered chalcogenides, with a stacking of the layer's perpendicular to the growth direction of the chalcogenide NTs. Parallel platelet-like segments appear in an alternating periodic manner along the growth direction of the stacks. The layers within the stacks

are generally smooth. Apparently, the layers tend to bend between each segment at a length scale of about 5 nm. EDX reveals the presence of both niobium and tungsten. A closer view of the layers reveals diffuse bending and kinking that increase along the edges of the stacks (figure 3) while the whole structure remains straight. Kinks, interruption of layers, orthogonal faults, and low-contrast areas are common observed. The formation of all these defects can be related to the large compressive lateral lattice mismatch strain between NbS<sub>2</sub> and WS<sub>2</sub> during their growth. Substituting approximately 30% of niobium by tungsten leads to the formation of stacked NWs due to internal strain, rather than to the formation of Nb-doped Nb<sub>x</sub>W<sub>1-x</sub>S<sub>2</sub> NTs.



**Figure 3** TEM and HRTEM images of pure niobium oxide nanorods and tungsten oxide-coated niobium oxide and the product obtained after sulfidization of tungsten oxide-coated niobium oxide nanorods. (a) TEM image of the Nb<sub>2</sub>O<sub>5</sub> NWs obtained after the sol-gel process and (b) HRTEM image of a single NW obtained from the sol-gel process. (c) After solvothermal treatment the niobium oxide NWs were fully covered with tungsten oxide. (d) HRTEM image of a niobium oxide NW partially covered with tungsten oxide. (e-h) HRTEM images of the CRNWs. (e and f) High-resolution images showing the curving of the layers along the segments. (g and h) Periodic alternation along the stack.

#### 4. CONCLUSIONS

Recently, it was reported the first field-effect transistor consisting of a 2D single layer of the semiconductor MoS<sub>2</sub> as a conductive channel and HfO<sub>2</sub> as a gate insulator. The device exhibited a current on/off ratio at room temperature with mobility close to that achieved in thin silicon films or graphene nanoribbons. Therefore, metal chalcogenides monolayers gated by metal oxides epitaxially connected to conductive metals might exhibit interesting properties that require thin transparent semiconductors such as energy harvesting and optoelectronics.

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