SYNTHESIS, CHARACTERIZATION AND APPLICATION OF WS₂ NANOWIRE-NANOFILAKE HYBRID NANOSTRUCTURES

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Abstract

Transition metal dichalcogenide (TMD) materials crystalize in a layered structure with a stoichiometry MX$_2$ where M is a transition metal (Mo, W, Tc, Re, V, Nb, Ta, Ti, Zr, Hf) and X is a chalcogen (S, Se, Te). While there is a strong covalent bond between the chalcogen and the metal atoms in each 2-dimensional (2D) sheet, the bulk 3-dimensional crystals are held together by weak van der Waals forces acting on the adjacent 2D sheets allowing for micromechanical and liquid phase exfoliation into nanostructures composed of either a single layer or a few layers. Since the electronic band structure depends not only on the chemistry but also on the number of layers, a whole new range of metal, semimetal and semiconductor materials may be achieved. These properties, among many other advantages (e.g. tunable band structure, high mobility of carriers, easy intercalation with ions), make TMDs appealing and timely for applications in solar cells and photodetectors, heterogeneous catalysis, electrocatalytic electrodes, energy storage and in (electro) chemical sensing. Motivated by the anticipated fascinating properties of TMDs, this research work focuses on the synthesis, characterization and application of a novel hybrid WS$_2$ nanomaterial. While the original goal of the research work was to develop a simple method to synthesize WS$_2$ nanowires, it became clear that instead of nanowires a hybrid nanowire-nanoflake (NW-NF) structure could be synthesized by a simple thermal sulfurization of hydrothermally grown WO$_3$ nanowires. The structure, morphology and composition of the new materials were analyzed by X-ray diffraction, Raman spectroscopy, electron microscopy and X-ray photoelectron spectroscopy. Temperature dependent electrical measurements carried out on random networks of the nanostructures showed nonlinear characteristics and a negative temperature coefficient of resistance indicating that the hybrids were semiconducting. Resistive gas sensors were prepared and exposed to H$_2$S, CO, NH$_3$, H$_2$ and NO and to which the devices displayed ultra-high sensitivity (0.043 ppm$^{-1}$) towards H$_2$S with a detection limit of 20 ppb. The results suggest further exploration of gas sensing with TMDs as potential competitive alternatives to the classical metal oxide based devices. Moreover, photodetector devices with excellent visible light response were also demonstrated using an individual WS$_2$ NW-NF hybrid as well as its random networks having photoresponsivity of up to 400 mAW$^{-1}$. This was two orders of magnitude higher than that measured for other 2D materials based devices. Overall, the WS$_2$ nanowire-nanoflake hybrid is a truly multipurpose and multifunctional semiconductor making it a promising material for advanced micro, nano and optoelectronics devices.

Keywords: gas sensor, nanoflake, nanohybrids, nanowire, photodetector, WO$_3$, WS$_2$
Asres, Georgies Alene, WS2-nanolanka-nanohiutale -hybridirakenteen synteesi, karakterisointi ja sovellukset.

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Asiasanat: kaasuanturi, nanohiutale, nanohybridit, nanolanka, valokenno, WO3, WS2
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Oulu, February 2018

Georgies Alene
List of original publications

This thesis is based on the following three original publications:

I

II

III

The synthesis methods used to obtain WS2 nanowire-nanoflake hybrid materials and their characterization are reported in Paper I. Specifically, a gas-phase sulfurization method is developed to synthesize the WS2 nanohybrid materials from hydrothermally grown WO3 nanowires. To assess the chemical composition, micro and crystal structure as well as the electrical and optical properties of the synthesized new nanomaterials, a broad range of analytics including X-ray photoelectron spectroscopy (XPS), scanning and transmission electron microscopy (SEM and TEM), X-ray diffraction (XRD), Raman spectroscopy are applied, as well as temperature dependent 2- and 4-point probe current-voltage (I-V) measurements.

In Paper II, resistive gas sensors based on drop-cast WS2 nanowire-nanoflake networks are demonstrated on lithographically defined Si chips. The sensor sensitivity for five different analyte gases (CO, H2, NH3, H2S and NO) are measured and evaluated at 30°C and 200°C. The results reveal the sensors have excellent sensitivity and selectivity towards H2S gas. To shed light on the interaction of H2S with the WS2 sensing element ab initio calculations are carried out. The Badar analysis indicates that the local charge transfer between the analytes and pristine WS2 is very small, and thus suggests that the excellent sensitivity towards H2S observed in the experimental study might be due to a different phenomenon. XPS is implemented to study further the possible origin of the high sensitivity of the sensor towards H2S. The XPS study shows that O2 in the environment during the gas sensing measurements induces a partial (and reversible) substitution of S with O at the anionic sites of the lattice. This is then reset in the presence of S in the ambient
giving a reasonable qualitative explanation for the chemoresisstive properties of the material.

Paper III reports on photosensor devices constructed from individual WS$_2$ nanowire-nanoflake hybrid materials electrically connected to sputtered Pt probe pads using FIB deposited Pt wires. The sensors are illuminated by three different lasers (401 nm, 552 nm and 661 nm) tuned between 1 and 100 mW power to evaluate the spectral and power dependence of the photoresponse. The measured highest responsivity $\sim$400 mA·W$^{-1}$ is significantly better than most TMDs or early reported graphene based photodetector devices.

The experiments such as materials synthesis, XRD, Raman, EDS and SEM analysis and gas sensing measurements were carried out by the Author. Optical measurement for the optical band gap calculation was performed by Dr. Alexey Popov. Electrical and HR-TEM analyses were jointly conducted by Aron Dombovari, Sami Saukko, Teemu Sipola and Dr. Jhih-Fong Lin. Photoconductivity measurements were performed by the Author with the kind assistance of Topias Järvinen. FIB processing was carried out by Esa Heinonen. XPS measurements were performed by Dr. Andrey Shchukarev (Umeå University). First-principles calculations were conducted by Dr. José J. Baldovi, Dr. Lede Xian, Dr. Alejandro Pérez Paz and Prof. Angel Rubio (Universidad del Pais Vasco and Max Planck Institute for the Structure and Dynamics of Matter). Conductive AFM analysis was carried out by Dr. Gabriela S. Lorite. Finite-element simulations were done by Dr. Geza Toth (VTT Technical Research Centre of Finland). The experiments were planned by Prof. Krisztian Kordas. The manuscripts were written by the Author with the kind help of all co-authors.
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1 Motivation, objectives and outline of the thesis

Among the different transition metal dichalcogenide materials, in this work, tungsten disulfide (WS₂) nanowire-nanoflake hybrid was synthesized, investigated and applied in a number of different applications. Although the chemical and atomic structure of WS₂ are similar to those of molybdenum disulfide (MoS₂), WS₂ has received less attention than MoS₂. However, similarly to MoS₂, WS₂ also has interesting properties such as layer number dependent electrical and optical properties as well as catalytic, electrocatalytic and photocatalytic activity making it a promising material for diverse applications [1].

The new nanowire-nanoflake hybrid material developed in this work, in which nanoflakes protrude from the surface and are thus an integral part of the nanowires, may combine the unique structural and electronic properties of one dimensional nanowires and the outstanding properties of two dimensional nanoflakes. The above mentioned reasons are the major motivations behind the synthesis and characterization of WS₂ nanostructure in this research with the hope of finding at least a few functionalities having practical importance or which can benefit the development of other similar materials and devices.

New types of semiconducting materials are needed for future electronics devices that may be based on the new materials alone or in combination with existing ceramic, polymer or Si platforms. Novel types of transistor materials, which enable a high channel current on/off ratio and fast switching demand high carrier mobility, scalability to nanoscopic dimensions and compatibility with C-MOS technologies [2]. Two dimensional materials, mainly TMDs, fulfill several of these requirements and may complement or even compete with existing classical 3D electronic materials. They are very thin, which supports efficient control over switching and can help to decrease short-channel effects and power dissipation, the main factors limiting transistor miniaturization [2]. This suggests that WS₂, one of the common TMDs, is a promising material for field effect transistors (FETs) and thus gives encouragement to fabricate and study the new WS₂ nanohybrid as a channel material.

On the other hand, being nanostructured, the semiconducting WS₂ nanohybrid is expected to have a large specific surface area and is known to exhibit some catalytic behavior, prompting its analysis for gas sensing applications. To address this hypothesis, simple Taguchi-type resistive gas sensor devices have been produced, their properties measured, and the results assessed in the light of
previously reported [3] and revisited theoretical data obtained by first principles calculations.

Further, again because of the material’s semiconducting nature with a low band gap, it is anticipated to have some functionalities that may be exploited for optoelectronics using visible light. For this purpose simple photosensor devices based on individual particles of the nanohybrid were also prepared and studied.

Accordingly, the objectives of this thesis were to develop a simple method to synthesize WS\(_2\) nanostructures, and after exploring their chemical and physical properties, to find some relevant applications in micro and nanoelectronics.

The corresponding work is summarized in this thesis using the scheme as follows: After the introductory section describing the properties, synthesis methods and applications of TMDs (Chapter 1), the details of experiments are given in Chapter 2, which is followed by the major findings and their discussion in Chapter 3. Finally, the thesis is summarized and the implications of the work are concluded in Chapter 4.
2 Introduction

2.1 Inorganic layered transition metal dichalcogenide nanostructures

The recent rapid developments in electronics, medicine, health care, energy production, environmental remediation and transportation have been fostered with the help of new nanomaterials and associated technologies. Among the new materials, owing to their layered structure and promising physical and chemical properties [4] inorganic layered transition metal dichalcogenides (TMDs) represent an important and fascinating family of nanomaterials.

Although all group 16 chemical elements (i.e. the oxygen group) of the periodic table are defined as chalcogens, the term chalcogenides is commonly reserved for sulfides, selenides and tellurides. In brief, TMDs are a group of materials with a formula MX$_2$, where M is a transition metal (Mo, W, Tc, Re, V, Nb, Ta, Ti, Zr, Hf) and X is a chalcogen (S, Se, Te). TMDs of groups 4-7 metals tend to crystallize in layered structures, while those in groups 8-10 are commonly found in non-layered structures [5]. In each layer, the metal and the chalcogen are covalently bonded on both sides (see Figure 1a). These covalent bonds provide the structural integrity of a single layer. To form a bulk crystal, several layers are held together by weak van der Waals forces acting between adjacent chalcogen slabs. Due to this weak inter-plane interaction it is easy to separate this material by micromechanical and liquid phase exfoliation, even allowing the isolation of single layers [6]. TMDs have a hexagonal or rhombohedral symmetry, and the coordination of the metal atoms are octahedral or trigonal prismatic. [2]

![Fig. 1. Schematic representation of a typical MX$_2$ structure, with the chalcogen atoms (X) in yellow and the metal atoms (M) in black [2]. The monolayer comprises a metal layer sandwiched between two chalcogen layers in a trigonal prismatic arrangement, forming an X-M-X structure.](image-url)
TMDs exhibit remarkably diverse electronic properties that can display a metallic, semiconducting or even a superconducting nature, i.e. all the kinds of electronic materials we use in daily life (See detail in Table 1). Nanoscale TMDs are rapidly emerging with new discoveries of their unique optical, electronic, catalytic and mechanical properties [7]. Interestingly, their electron structure and optical properties are layer number dependent. For instance, WS$_2$ changes from indirect gap (1.4 eV) [2] to direct gap (2.1 eV) when the bulk sample is reduced in size to a monolayer. The possibility of creating single or several stable atomic-thickness layers of these materials was realized following the success of graphene, although practical applications of graphene as a zero band gap semiconductor are limited without additional manipulation [2]. Different approaches have already been implemented to engineer the band gap in graphene, such as using nanostructuring [8,9], chemical functionalization [10], and the application of extreme external fields [11]. However, these methods have the drawback of adding complexity and diminishing carrier mobility [2]. This is where semiconducting TMDs with a finite band gap can complement or even compete with graphene. Furthermore, as it is possible to tune their electronic structure by simply varying the chemical composition and particle geometry, TMDs hold great promise for nano and optoelectronics [12].

Although there have been very many studies reporting the electronic and other relevant properties of graphene and its derivatives, layered TMDs are just emerging, and materials other than MoS$_2$ have not been given deep coverage. Furthermore, suitable methods for the large scale synthesis of layered semiconductors are yet to be developed. This research work attempts to bridge these gaps by focusing on synthesis, characterization and some potential applications of WS$_2$ nanostructures.

**Table 1. Electrical properties of TMDs.**

<table>
<thead>
<tr>
<th>Group</th>
<th>Transition Metal</th>
<th>Chalcogen</th>
<th>Properties</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Ti, Hf, Zr</td>
<td>S</td>
<td>Diamagnetic semiconductors (E$_g$: 0.2-2.0 eV)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Se</td>
<td>Diamagnetic semiconductors (E$_g$: 0.2-2 eV)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Te</td>
<td>Diamagnetic semiconductors (E$_g$: 0.2-2 eV)</td>
<td></td>
</tr>
</tbody>
</table>
Group | Transition Metal | Chalcogen | Properties | Reference
--- | --- | --- | --- | ---
5 | V, Nb, Ta | S | VS₂ (ferromagnetic semiconductor), NbS₂ (nonmagnetic metal), TaS₂ (semiconductor) \( \rho \approx 10^{-4} \, \Omega \text{cm} \) | 13-17
 | Se | | VSe₂ (ferromagnetic, narrow band metals), NbSe₂ (metallic), TaSe₂ (semimetal) | |
 | Te | | VTe₂ (ferromagnetic), NbTe₂ (superconducting) | |
6 | Mo, W | S | Semiconducting diamagnetic \( E_g \approx 1 \) eV | 18
 | Se | | Semiconducting diamagnetic \( E_g \approx 1 \) eV | |
 | Te | | Semimetallic \( \rho \approx 10^{-3} \, \Omega \text{cm} \) | |
7 | Tc, Re | S | Small gap semiconductors. Diamagnetic | 18
 | Se | | Small gap semiconductors. Diamagnetic | |
 | Te | | Small gap semiconductors. Diamagnetic | |
10 | Pd, Pt | S | Sulfides (PdS₂, PtS₂) semiconducting and \( E_g \approx 0.4 \) eV | 18-20
 | Se | | PdSe₂ (semiconducting), PtSe₂ (semimetal) | |
 | Te | | PtTe₂ (metallic) and PdTe₂ (superconducting) | |

Symbol \( \rho \) denotes in-plane electrical resistivity.

### 2.2 Synthesis of TMDs

Chemical vapor deposition (CVD) and doping are arguably among the best methods to prepare nanostructured materials and thus these techniques have been under intense development in the last two decades. Being compatible with existing semiconductor technologies, scalable and economically competitive, these methods are key to the fabrication of many industrial products [21]. In a typical CVD process, inside a reactor, source gases containing the precursors are transported towards a substrate. With energy supplied by either heating or plasma discharge, the precursors decompose and/or react with each other and a thin film of product forms on the substrate. The spent gases are removed by gas flow through an outlet. Doping is similar in terms of apparatus but the reaction takes place between a solid phase and the vapor of doping atoms or their precursors, thus...
facilitating doping and/or chemical reaction at elevated temperatures in which the chemical composition (and sometimes also the microstructure) of the solid changes. When the doping process is excessive, practically all of the atoms in the anionic (or cationic) sites can be replaced.

One of the first studies into the formation of polyhedral and cylindrical WS$_2$ nanowires (or one dimensional WS$_2$) was reported in 1992 [22]. These nanostructures were achieved by heating thin tungsten films in an atmosphere of hydrogen sulfide. Since then, several recipes have been shown to produce sulfide nanostructures using a strategy that involves heating (or even evaporation) of metals or their oxides in sulfur vapor or H$_2$S gas. Recently, WS$_2$ nanotubes decorated on their outer surface with fullerene-like WS$_2$ nanoparticles have been produced by sulfurizing W$_5$O$_{14}$ (WO$_{2.8}$) nanowhiskers [23]. Reproducible mass production (a few 100 g/batch) of a pure WS$_2$ nanotube phase using a large fluidized bed reactor was also demonstrated by annealing mixtures of different WO$_x$ (2.83 $\leq$ x $\leq$ 3) phases and morphologies in H$_2$S and H$_2$/N$_2$ at 800-900°C [24]. Synthesis of WS$_2$ and WSe$_2$ nanowires on stainless steel using metallic tungsten and chalcogen powder as precursors under autogenic pressure at 750°C has also been demonstrated [25]. WO$_3$ nanorods annealed in H$_2$S at 840°C resulted in the formation of multi-walled WS$_2$ [26]. MoS$_2$ and WS$_2$ onion-like nanoparticles and three dimensional nanoflowers were produced by atmospheric pressure CVD with the reaction of chlorides (MoCl$_5$/WCl$_6$) and sulfur [27]. Under optimized conditions of deposition temperature, sample position in the reactor and flux of the carrier gas, control over the synthesized product morphologies was demonstrated. In other work [28], WS$_2$ flakes on Si wafers were synthesized using a low-pressure chemical vapor deposition technique. It was shown that with a proper positioning of S and WO$_3$ precursors and the growth substrate in three different zones of the furnace, and adjustment of other growth parameters (e.g. the time of S precursor introduced, the temperature of WO$_3$ precursor and deposition temperature) the morphology of the WS$_2$ product could be tuned.

In this thesis, a simple CVD method is developed to synthesize one dimensional WS$_2$ nanowires covered with two dimensional nanoflakes using hydrothermally grown WO$_3$ nanowires and sulfur as precursors. Since the shape and thickness of the WS$_2$ flakes can significantly influence their electronic, photoelectric and mechanical properties, [28] fascinating properties of the new WS$_2$ nanohybrids may be expected.
2.3 TMD based field effect transistors

Typically, smaller and faster electronic devices are currently realized by miniaturization of silicon based transistors [29]. However, some fundamental limits such as high leakage current, short channel effect, pronounced carrier and phonon scattering and contact resistance restrict any significant further improvement in the future. Moreover, the brittle nature of silicon limits its straightforward application in flexible electronics [30, 31]. Numerous efforts to overcome the above mentioned limitations have already been attempted using novel device architectures and alternative materials [32,33]. Semiconducting 2D TMDs are among the investigated and promising alternative materials. Properties such as structural stability, small band gap, lack of dangling bonds and thus high mobility compared to that of silicon make semiconducting 2D TMDs attractive for FET applications [34]. In 2004 Podzorov et al. reported [35] WSe2 crystals with p-type conductivity and carrier mobility as high as 500 cm²V⁻¹s⁻¹ at room temperature. The above result was soon followed by bottom gated FETs using a thin layer of MoS2 as a channel material having mobility values in the range of 0.1-10 cm²V⁻¹s⁻¹ [2, 36] and a high ~10⁴ on/off ratio measured at 60 K.

2.4 Photodetectors and other optoelectronic devices

Photodetectors are ubiquitous devices with the main function of collecting and converting information associated with light into electrical signals that can be processed by standard electronics. Among different materials, silicon based photodetectors are preferred because of their compatibility with complementary metal–oxide semiconductors (CMOS) technology that enables device miniaturization and scalability at affordable cost. However, in order to make color sensitive silicon devices, it is necessary to use filters. In addition, silicon’s indirect band gap reduces the photoefficiency. Therefore, the industry and scientific communities are expending considerable efforts to find novel nanoscale materials that may complement or even compete with traditional Si, Ge, GaAs and other compound semiconductors [37].

Semiconducting layered TMDs, with their layer number and composition dependent electronic structure, make it possible to select any predefined band gap thus enabling detection of light in different spectral regions [38]. Furthermore, owing to the direct band gap of several compositions and structures, fast and efficient detectors may be achieved. Accordingly, in recent years, intense research
into the understanding and engineering of the optoelectronic properties of TMDs and related devices has been started [37]. With respect to this, there are some properties of WS$_2$ that makes it even more interesting than other semiconducting TMDs. Firstly, WS$_2$ displays ambipolar field modulation behavior[38,39] and its suitably reduced (hole and electron) effective mass, as found by theoretical study, enables a high carrier mobility[40]. For instance, recently a field effect mobility of 234 cm$^2$ V$^{-1}$ s$^{-1}$ has been measured for multilayer WS$_2$ at room temperature using direct Au contacts [41]. Secondly, compared to MoS$_2$ crystals, monolayer WS$_2$ has approximately a twenty-fold greater photoluminescence emission intensity [42] which promises optoelectronic devices with a relatively high quantum efficiency.

Similar to other applications of TMDs, most of the reports refer to MoS$_2$ and only very recent studies have shown that tungsten disulfide is also a promising material for photodetectors, such as CVD grown WS$_2$ nanoparticle thin films [43], a CVD grown monolayer WS$_2$ photodetector with graphene electrodes [44] and a monolayer WS$_2$ phototransistor [45,46].

2.5 Gas sensors

The environment around us is composed of different gases with various properties, origins and concentrations. Some are toxic while others are vital for life or indicators of health. Accordingly, gas sensors are needed in different applications such as environmental protection, industrial process monitoring and safety, amenity, energy saving, health, foods, and so on [47]

Studies concerning semiconductor gas sensors undertook a considerable expansion in the late 1980s, and became one of the most active research areas within the sensor community [47]. Among them, metal oxide semiconductors stand out as the ones most commonly used. The recent rapid progress in nanotechnology and materials science resulted in new nanomaterials and devices that extended the field of semiconducting gas sensors [48-51]. Metal oxide semiconductor based gas sensors have high sensitivity, particularly at high temperatures, but one of their drawbacks is their poisoning and deactivation by even the smallest traces of sulfur or its compounds. Further, to achieve selectivity for a particular analyte, it is necessary to sensitize them e.g. by decorating the oxide surface with various metals or other metal oxides [52]. Due to these reasons and to improve further the existing sensing performance, scientists are trying different approaches to substantiate new frontiers of materials for gas sensing including carbon nanotubes [53], graphene
[54], conducting polymers [55] and lately, transition metal dichalcogenide nanostructures [56].

Research results suggest that charge transfer based conductance modulation [3, 56, 57, 58] is the working mechanism of these sensors. Since the electronic density of states is dependent on the dimensions of the crystal lattice, it is reasonable to speculate that gas sensing properties are also influenced by the dimensions and microstructure of the sensing material. This gives the main motivation to investigate the gas sensing properties of one dimensional WS$_2$ covered with two dimensional nanoflakes in this study.
3 Materials and methods

3.1 Materials synthesis

The starting material WO₃ for synthesizing WS₂ was achieved by a hydrothermal process. 18.74 g of Na₂WO₄·2H₂O (Sigma-Aldrich, ACS reagent 99%) and 22.49 g of Na₂SO₄ (Sigma-Aldrich, ACS reagent ≥99.0%) were dissolved in 600 mL distilled water and the pH = 1.5 was adjusted using 3 M HCl solution. After 10 min stirring, the solution was transferred to an autoclave (Parr Series 4520 Bench Top Reactor with PTFE lining) and stirred (35 rpm) for 48 h at 180°C under autogenic pressure. The product suspension was collected, centrifuged (Hettich, Universal 320, 20 min, 3000 rpm), washed with distilled water and ethanol and then dried at 60°C for 24 h.

WS₂ nanomaterials were obtained by sulfurization of the WO₃. Sulfur powder (1.0 g, reagent grade, purified by sublimation) and WO₃ nanowires (0.1 g) were placed in two different alumina boats at the center of a tubular reactor. Before sulfurization, the reactor was evacuated to a base pressure of ~1 torr and filled with N₂ at 1 bar. The evacuation and flushing steps were repeated three times to minimize O₂ in the reactor. Sulfurization was performed for a period of 10 min at 500, 600, 700 or 800°C in a flow of 400 sccm N₂. The product synthesized at 800°C was used for the investigations.

3.2 Structural and chemical characterization

The synthesized products were analyzed by the means of X-ray diffraction (Bruker D8 Discovery, Cu Kα), micro-Raman spectroscopy (Horiba Jobin-Yvon Labram HR800 at λ = 488 nm), scanning electron microscopy (FESEM, Zeiss Ultra Plus) and transmission electron microscopy (FEI Tecnai G2 20 X-Twin at 200 kV acceleration) to investigate the crystal structure and microstructure of the materials. X-ray photoelectron spectroscopy (monochromatic Al Kα source operated at 150 W) equipped with a delay line detector and a charge neutralizer was conducted to examine in detail the elemental compositions and oxidation states.
3.3 Optical characterization

The optical properties of the powder samples were studied using a spectrophotometer system (Optronic Laboratories, USA) equipped with an integrating sphere. The powder was mounted on a microscope slide with double-sided scotch tape. The total reflectance from the scattering powder was measured within the 400-1100 nm spectral range. Subsequently the optical absorption was calculated, from which the optical band gap of the products prepared under different conditions was derived.

3.4 Electrical measurements

For the I-V measurement (two-point probe and four-point probe), Pt electrodes were defined by photolithography on top of an SiO\textsubscript{2}/Si wafer. The WS\textsubscript{2} nanowire-nanoflake hybrid was dispersed in acetone and drop cast to bridge the interdigital Pt electrodes. Then the electrodes were probed under a probe station (Wentworth labs station) connected to a computer-controlled source meter (Keithley 2636A) and the I-V curve was measured. The measurement was conducted at room temperature in ambient air.

Field effect transistors (FETs) were fabricated using conventional photolithography techniques in a clean room using the WS\textsubscript{2} NW-NF hybrid as a channel material. The procedure was as follows. A SiO\textsubscript{2}/Si wafer (consisting of a thermally grown 300 nm oxide film on Si) was purchased. Then the interdigital Au/Ti layer was defined by photolithography on top of the insulating SiO\textsubscript{2} layer. On the reverse side an Al/Ti/Au multilayer was deposited consecutively by sputtering (as a back gate contact). The WS\textsubscript{2} NW-NF hybrid material dispersed in acetone was then drop cast on the front side between the gold electrodes as a channel. Then the back gated FET device was ready for test. The gold contacts on the front sides and the gold on the reverse were probed in the probe station and electrical and optical measurement performed using a computer-controlled Keithley 2636A source meter.

The output and transfer characteristics curves of the FETs were measured using a probe station. A LabVIEW script was developed for this purpose. In addition, the photosensing properties of the FET were investigated by illuminating the sample with a light emitting diode (LED). A standard collimated RGB light-emitting diode was used (emission centered at 623 nm, 517.5 nm and 466 nm with corresponding...
luminosity values of 800, 4000 and 900 mcd, respectively; chip-to-diode distance of 5 cm at an illumination angle of ~45°).

3.5 Gas sensor device fabrication and measurements

Resistive type gas sensors were fabricated as follows. First, platinum electrodes were defined by photolithography on the front side of the SiO₂/Si wafer in a similar manner to that discussed above in section 2.4. Then, the WS₂ sensing material was dispersed in acetone and drop cast between the Pt finger electrodes. The platinum electrode probed by the contact needles of the probe station enabled the subsequent electrical and gas sensing analyses. All the prepared devices were dried overnight in ambient air before the gas sensing measurements to desorb moisture and stabilize the base resistance of the sensor. The gas sensing measurements were conducted using a Linkam heating and freezing stage. The sensors were investigated upon exposure to five different analyte gases (H₂S, CO, NH₃, H₂ and NO) with nominal concentrations between 1 and 600 ppm, adjusted using MKS type 247 mass-flow controllers. For the H₂S gas sensing measurements, lower gas concentrations were also applied between 10 and 1000 ppb. All measurements were performed in air buffer at 30°C and 200°C. A LabVIEW script was used to control the temperature and gas concentration by computer during the gas sensing measurements. The resistance of the sensors was monitored by an Agilent 3458 multimeter using a constant bias of 1V.

3.6 Photosensor device fabrication and characterization

Photosensor devices were prepared using individual particles of WS₂ NW-NF hybrids. A Si/SiO₂ wafer was cut with a laser into 7×7 mm squares. A TEM grid was taped on the top of the chip and 200 nm thick Pt was deposited by sputtering (using the grid as a shadow mask) to define the probe pads. After that WS₂ dispersed in acetone was drop cast on the surface and Pt nanowires were deposited on the surface by the means of focused-ion beam-assisted CVD to connect the individual WS₂ structures to the sputtered Pt pads. The Pt contact pads were probed in the (photo) electrical measurements using a probe station. The photo sensing data were averaged over 16384 measurement sets. For the photo sensing measurements a Coherent® High-Performance OBIS™ Laser System (TEM00 mode, λ=661, 552 and 401 nm with a corresponding 1/e² beam diameter of 9, 7 and 8 mm) was used to illuminate the samples. The laser beams were modulated with a
10 kHz square wave signal from a signal generator (TGA1244, Thurlby Thandar Instruments Ltd.). The device was connected in series with a 19.6 MΩ load resistance and probed with an oscilloscope (Agilent InfiniiVision DSO-X 3024A, Agilent Technologies, Inc.). The 10 MΩ oscilloscope probe (Agilent N2863B, Agilent Technologies, Inc.) formed a parallel resistor circuit with the load resistor resulting in a net impedance of 6.62 MΩ. A synchronization signal was used for triggering the measurement with the laser. The photocurrent and responsivity of the devices were evaluated as a function of laser power (1, 2, 5, 10 and 20 mW at all wavelengths plus 50 mW at 401 nm as well as 50 and 100 mW at 661 nm).
4 Results and discussion

4.1 The structure of the synthesized materials (Paper I)

In Paper I, hydrothermally grown WO₃ nanowires and sulfur powder were used as precursors to synthesize WS₂ nanostructures at four different temperatures (500°C, 600°C, 700°C and 800°C). The morphology of the synthesized WO₃ nanowires and the products after sulfurization are shown in Figure 2 (a-e). The diameter of the WO₃ nanowires was found to be between 270 and 390 nm and their length varied between 1-3 µm. The effect of sulfurization on the morphology of the product was insignificant at 500 and 600°C, whereas tiny flakes appeared on the surface at higher temperatures. Thus, the products synthesized at 700°C and above had features of both one and two dimensional materials combined in a single nanostructured particle.

![Fig. 2. Structural change of WO₃ during sulfurization.](image)

The crystal structure of the original material was hexagonal according to XRD [data sheet PDF 01-075-2187]. The sulfurized products showed a different diffraction pattern at higher temperature suggesting the conversion of the original hexagonal WO₃ to hexagonal WS₂ (see Figure 2(f)). From the relative intensity of the most
intense peaks (e.g. at 28.2° and 36.6° corresponding to the (200) and (201) planes of WO$_3$, and the (002) and (103) of WS$_2$ at 14.4° and 39.6°, respectively), it was found that the WO$_3$ phase dominated up to 500°C but the samples produced above this temperature were dominantly hexagonal WS$_2$ [data sheet PDF#841398], with an apparently complete WO$_3$ to WS$_2$ conversion at 800°C. Since this work was concentrated on metal dichalcogenides, all subsequent discussion is focused on the WS$_2$ product produced at 800°C.

Transmission electron microscopy (TEM) was employed to investigate the micro and nanostructure of the WS$_2$ products. In Figure 3(a), flakes surrounding the nanowire are visible, thus the name of the nanostructured particle *hybrid nanowire-nanoflake*. Analysis of the distance between the fringes of the thin flakes (Figure 3(b)) gave 0.62 nm, which is consistent with the (002) d-spacing for the layered WS$_2$ structure. Figure 3(d) shows the selected area electron diffraction that indicated that the product was indeed hexagonal WS$_2$, agreeing well with the XRD result. In addition, TEM analysis revealed that the thickness of the 2D structures was below 10 nm, implying that the number of layers in the flakes was 15 or less. The EDS result supports the argument concluded by XRD regarding the conversion of WS$_2$ at 800°C.
Fig. 3. Structure of WS₂ hybrid materials. (a) Low magnification transmission electron micrograph of WS₂ nanowire-nanoflake hybrid synthesized at 800°C. (b) High-resolution micrograph of a flake with layered crystal structure. Inset shows the d-spacing of the layers. (c) SAED pattern of the WS₂ nanowire-nanoflake hybrid material. (d) Raman spectrum of the corresponding WS₂ nanowire/nanoflake hybrid material. (e) Raman spectroscopy of pristine WO₃ nanowire. (Paper I).

The Raman spectrum of the WS₂ nanowire-nanoflake hybrid prepared at 800°C (Figure 3 (d)) showed two significant peaks that matched the in-plane E₂g mode at (~352 cm⁻¹) and the out-of-plane A₁g mode at (~420 cm⁻¹) of crystalline WS₂. For comparison, the Raman spectrum of WO₃ is also included (Figure 3 (e)) displaying characteristic peaks centered at 242 cm⁻¹, 325 cm⁻¹ (bending modes of O-W-O) and at 668 cm⁻¹, 810 cm⁻¹ (stretching modes of O-W-O).[59] [60][61]

4.2 Electrical properties and light sensing behavior of WS₂ nanohybrid networks (Paper I)

The electrical properties of WS₂ nanowire-nanoflake hybrid networks exhibited a nonlinear current-voltage characteristic as shown in Figure 4(a) in both 2- and 4-point measurement arrangements. In the 4-point probe setup, the effect of any possible barrier caused by the WS₂-Au interface was excluded but the I-V curve was still nonlinear and might be attributed to the contacts between the nanohybrids in the random networks. The resistance of nanohybrids measured in air showed a decrease with increasing temperature (Figure 4(b)) that implied the product was
semiconducting. The data could be well fitted by both thermal activation and variable-range hopping (VRH) models. Evaluating the fitting parameters however, it was found that thermal activation was probably the best mechanism to describe the conduction process with an apparent activation energy of 0.29 eV (see inset in Figure 4(b)), as the fitting parameters for the VRH model are non-physical.

Fig. 4. (a) Current-voltage characteristics (2- and 4-point probe) and temperature dependent resistance (2-point probe) of WS₂ hybrid films. Inset in panel (b) displays the corresponding Arrhenius plot for the thermally activated conduction. (Paper I).

Back-gated field effect transistor (FET) measurements of the networks of products synthesized at different temperatures showed no field effect at all for the materials obtained at 500°C or 600°C. On the other hand, a FET prepared using the sample synthesized at 800°C displayed a small but measurable field effect as shown in Figure 5 (a) with a corresponding field effect mobility of 0.02 cm² V⁻¹ s⁻¹. The obtained value is reasonable and comparable to MoS₂ and WS₂ based FET (0.004-0.04 cm² V⁻¹ s⁻¹) [62, 63] and CVD grown MoS₂ [64] or CVD grown WS₂ [65]. It was assumed that the obtained low field effect mobility was caused by the large numbers of contacts between the nanowires in the nanowire network. If so, there is a possibility to improve the field effect mobility by using very few or individual WS₂ nanoparticles in the channel. This argument is supported by experimental results published for single crystal WS₂ with ~20 μm crystal size (100 cm² V⁻¹ s⁻¹) [66] and for WS₂ films (9–15 cm² V⁻¹ s⁻¹) [67]. Taking this into consideration, a low density nanowire-nanoflake based FET was prepared and its output characteristics and transfer curves were measured. Consistent with the above assumption, the field effect mobility showed one order of magnitude improvement (0.18 cm² V⁻¹ s⁻¹), as displayed in Figure 5 (b). While the high contact resistance between the nanowires in the network was expected to be the major reason for the poor gate effect, the high thickness of the SiO₂ (300 nm) used in the experiments could also be
responsible for such poor behavior. An additional investigation reducing the oxide layer thickness (< 100nm) is required before any further conclusions can be drawn.

Fig. 5. Output characteristics of the WS₂ nanowire nanoflake hybrid based FET devices. Current-voltage curves for (a) high and (b) low density random networks of the hybrid nanowires between the source and drain electrodes. Inset in panel (a) displays a magnified plot for the outlined regime between 4.4 and 4.5 V for better visibility of the current values at different gate voltages. Inset in panel (b) shows a dark field optical micrograph of a device. (Paper I).

To obtain information about the optical properties of the product, the total reflectance of films made of the nanostructures was measured, and the band gaps calculated from the corresponding Tauc plots (Figure 6(a)). The results, clearly indicating that the band gap of WO₃ nanowires dropped from 2.6 eV to 1.4 eV as a result of sulfurization, are in good agreement with the literature data [68].

Fig. 6. (a) Tauc plot for direct band-to-band transition derived from total reflectance measurements on the original and sulfurized powders. Dashed lines represent fitting of the linear sections of each curve. Intersections of the dashed lines with the horizontal axis define the band gap. (b) Current-voltage characteristics of a high density FET under different LED illumination conditions (red, green and blue centered at 623 nm, 517.5 nm and 466 nm, respectively). (Paper I).
In addition to the electrical characterization, the FET was illuminated by light emitting diodes (LEDs) to assess the photoresponse of the material. As depicted in Figure 6 (b), the channel current was modulated by the LED illumination. Among the tested three different colors, the effect was somewhat more significant for blue light, probably due to the better optical absorption and more efficient photogeneration of carriers in the semiconductor as compared to the longer wavelengths.

4.3 Resistive gas sensing with WS\textsubscript{2} nanohybrid networks (Paper II)

Paper II focuses on using the synthesized WS\textsubscript{2} nanowire-nanoflake hybrid material as a gas sensing element in resistive (Taguchi-type) devices. The sensors were exposed to five different analytes (H\textsubscript{2}S, CO, NH\textsubscript{3}, H\textsubscript{2} and NO) at two different temperatures (30°C and 200°C). The three key performance indicators to assess gas sensor performance, response, sensitivity and recovery, were evaluated.

The sensors showed a positive/negative resistance response for reducing/oxidizing gases (Figure 7) indicating that WS\textsubscript{2} nanowire-nanoflake hybrids are p-type semiconductors and the possible working mechanism of the sensor is charge transfer conduction modulation, similar to other reported results [3,57, 69].
Fig. 7. Sensor response curves for (a) H\textsubscript{2}S, (b) CO, (c) NH\textsubscript{3}, (d) H\textsubscript{2} and (e) NO in air buffer at ppm gas concentration levels measured at 30°C and 200°C. (Paper II).
The typical response times obtained were 1 and 2 min at 200°C and longer (3-6 min) at 30°C. Since reaction adsorption/desorption and reaction rates increase with temperature, the observed quicker response at 200°C was reasonable.

The sensitivity to H$_2$S was particularly high (0.023 ppm$^{-1}$) and prompted further testing of the WS$_2$-H$_2$S system in the ppb concentration regime (Figure 8). The detection limit of the sensor was found to be 20 ppb at 200°C with a corresponding sensitivity of 0.043 ppm$^{-1}$ i.e. the WS$_2$ nanohybrid was competitive with other known materials such as Fe$_2$O$_3$ nanochains and nanoparticles [70,71], CuO-SnO$_2$ [72], CuO nanoparticles [73] and nanosheets [74], mesoporous WO$_3$ [75], CeO$_2$ nanowires [76] and PbS quantum dots [77].

<table>
<thead>
<tr>
<th>Method</th>
<th>Sensing material</th>
<th>Sensitivity $^a$</th>
<th>Operating temperature</th>
<th>Lowest experimental H$_2$S concentration$^b$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistive</td>
<td>WS$_2$ nanowire-nanoflake hybrid</td>
<td>0.043 ppm$^{-1}$</td>
<td>200 ºC</td>
<td>0.02 ppm</td>
<td>This work</td>
</tr>
<tr>
<td>Resistive</td>
<td>α-Fe$_2$O$_3$ nanoparticles</td>
<td>~5.2 ppm$^{-1}$</td>
<td>300 ºC</td>
<td>0.05 ppm</td>
<td>[71]</td>
</tr>
<tr>
<td>Resistive</td>
<td>CuO nanosheets</td>
<td>~3.3 ppm$^{-1}$</td>
<td>240 ºC</td>
<td>0.03 ppm</td>
<td>[74]</td>
</tr>
<tr>
<td>Resistive</td>
<td>Mesoporous WO$_3$</td>
<td>~50 ppm$^{-1}$</td>
<td>250 ºC</td>
<td>0.25 ppm</td>
<td>[75]</td>
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<tr>
<td>Resistive</td>
<td>CeO$_2$ nanowire</td>
<td>~2 ppm$^{-1}$</td>
<td>Room temp.</td>
<td>0.05 ppm</td>
<td>[76]</td>
</tr>
<tr>
<td>Resistive</td>
<td>PbS quantum dots</td>
<td>~140 ppm$^{-1}$</td>
<td>135 ºC</td>
<td>10 ppm</td>
<td>[77]</td>
</tr>
<tr>
<td>Resistive</td>
<td>ZincO nanostructures</td>
<td>~0.14 ppm$^{-1}$</td>
<td>300 ºC</td>
<td>20 ppm</td>
<td>[78]</td>
</tr>
<tr>
<td>Resistive</td>
<td>Pt-loaded WO$_3$ thin films</td>
<td>~1200 ppm$^{-1}$</td>
<td>100 ºC</td>
<td>1 ppm</td>
<td>[79]</td>
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<tr>
<td>Resistive</td>
<td>Nanocrystalline In$_2$O$_3$-SnO$_2$</td>
<td>~20 ppm$^{-1}$</td>
<td>40 ºC</td>
<td>2 ppm</td>
<td>[80]</td>
</tr>
<tr>
<td>Resistive</td>
<td>SnO$_2$ thin film</td>
<td>0.2 ppm$^{-1}$</td>
<td>300 ºC</td>
<td>5 ppm</td>
<td>[81]</td>
</tr>
<tr>
<td>Resistive</td>
<td>SnO$_2$ nanocolumns</td>
<td>2.8 ppm$^{-1}$</td>
<td>300 ºC</td>
<td>5 ppm</td>
<td>[81]</td>
</tr>
<tr>
<td>Resistive</td>
<td>SnO$_2$ nanocolumns decorated with Au</td>
<td>22 ppm$^{-1}$</td>
<td>300 ºC</td>
<td>5 ppm</td>
<td>[81]</td>
</tr>
<tr>
<td>Resistive</td>
<td>SnO$_2$ nanocolumns decorated with Ag</td>
<td>12.8 ppm$^{-1}$</td>
<td>300 ºC</td>
<td>5 ppm</td>
<td>[81]</td>
</tr>
<tr>
<td>FET</td>
<td>Ultrathin Ph5T2 microplates</td>
<td>240 ppm$^{-1}$</td>
<td>Room temp.</td>
<td>0.5 ppm</td>
<td>[82]</td>
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<tr>
<td>FET</td>
<td>CuPc</td>
<td>0.004 ppm$^{-1}$</td>
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<tr>
<td>FET</td>
<td>Ir$_2$O$_3$ nanowires</td>
<td>0.41 ppm$^{-1}$</td>
<td>Room temp.</td>
<td>1 ppm</td>
<td>[84]</td>
</tr>
<tr>
<td>Method</td>
<td>Sensing material</td>
<td>Sensitivity</td>
<td>Operating temperature</td>
<td>Lowest experimental H₂S concentration</td>
<td>Ref.</td>
</tr>
<tr>
<td>--------</td>
<td>------------------</td>
<td>-------------</td>
<td>------------------------</td>
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</tbody>
</table>

* The highest sensitivity values were calculated from the published references as the relative change of electrical resistance normalized to the corresponding H₂S concentration i.e. \( \Delta R/(R_0 \cdot C_{H₂S}) \). When the electrical current values were reported, the sensitivity values were calculated from the relative change of the current at the corresponding gas concentration, i.e. \( \Delta I/(I_0 \cdot C_{H₂S}) \).

Fig. 8. H₂S sensing performance at ppb level. (a) Sensor resistance at 200°C. (b) Sensitivity of the five different sensors displaying high selectivity towards H₂S (0.023 ppm⁻¹ at 1 ppm according to data in Fig. 7). Data point labeled with an asterisk denotes sensitivity (0.043 ppm⁻¹) measured at 20 ppb H₂S. (Paper II).

To further elaborate the interaction of H₂S with WS₂ ab initio calculations were conducted using a simplified model that considered single and bilayer pristine undoped WS₂ [3]. The adsorption of each analyte on the surface was found to be thermodynamically stable (i.e. having negative adsorption energy). On the other hand, the adsorbed gases had little or insignificant contribution to the band structure in the band gap. Furthermore, Bader analysis suggested that a very small amount of charge was transferred for NH₃, NO and H₂S, and no sizable charge transfer at all for H₂ and CO. Accordingly, the modeling data indicated that the cause of the excellent sensitivity of the hybrids towards the H₂S molecule stemmed from a source other than direct charge transfer.

To reveal the changes of the surface chemistry in a typical H₂S sensing experiment, additional XPS analysis was conducted on three samples. Sample #1 represented an original WS₂ hybrid, Sample #2 represented materials that had undergone exposure to air at 200°C and Sample #3 was treated as Sample #2 but was subsequently also exposed to H₂S (at 200°C for 1 h in 1 ppm in air). The results shown in Table 3 reveal that when the WS₂ hybrid was heated in air, oxygen
partially substituted the surface sulfur. This could be reversed by inserting even 1 ppm H$_2$S into the gas. Therefore, the H$_2$S sensing process may be interpreted as reversible adsorption/desorption and red-ox reaction sequences, in which oxygen and sulfur compete for the anionic sites in the WS$_2$ lattice, resulting in a particularly high sensitivity of the material (and its electrical properties) for this analyte.

### Table 3. Surface composition of the WS$_2$ hybrid in various stages of the H$_2$S sensing process (Paper II).

<table>
<thead>
<tr>
<th>Line</th>
<th>Sample #1 (Original WS$_2$ hybrid)</th>
<th>Sample #2 (WS$_2$ hybrid heated in air)</th>
<th>Sample #3 (sample heated in air and subsequently in 1 ppm H$_2$S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE (eV)</td>
<td>FWHM (eV)</td>
<td>AC (at.%)</td>
<td>BE (eV)</td>
</tr>
<tr>
<td>C 1s</td>
<td>284.2</td>
<td>1.05</td>
<td>9.99</td>
</tr>
<tr>
<td>O 1s</td>
<td>530.6</td>
<td>1.35</td>
<td>9.7</td>
</tr>
<tr>
<td>Na 1s</td>
<td>1071.7</td>
<td>1.65</td>
<td>7.78</td>
</tr>
<tr>
<td>W 4f$_{7/2}$</td>
<td>32.7</td>
<td>0.65</td>
<td>18.49</td>
</tr>
<tr>
<td>S 2p$_{3/2}$</td>
<td>162.3</td>
<td>0.65</td>
<td>37.28</td>
</tr>
</tbody>
</table>

The aging effect is one of the concerns of the sulfide based nanomaterials. A recent study [85] revealed that WS$_2$ flakes undergo oxidation along their grain boundaries even at room temperature. However, there is no conclusive result regarding the long term aging effects [86].

#### 4.4 Photo sensing using individual WS$_2$ nanohybrid particles (Paper III)

Photodetector devices based on individual nanohybrid particles were prepared using FIB deposited Pt contacts and sputtered Pt probe pads (Figure 9(a)). Current-voltage curves measured for five different devices (Figure 9(b) showed linear behavior that indicated that the contacts were ohmic and there was good agreement with the Fermi level as well as the valence and conduction band positions of Pt and WS$_2$, respectively (inset in Figure 9(b)). [87-91].
Fig. 9. (a) SEM image of the individual WS$_2$ nanohybrid between platinum contacts, and (b) I-V curves of five devices with the corresponding band diagram of Pt-WS$_2$ contact.

The photosensitivity of individual nanohybrids was assessed at three different wavelengths (401 nm, 552 nm and 661 nm) between 1 and 100 mW total power (Figure 10). The photocurrent showed significant light intensity dependence and a rapid response of ~1 µs for each wavelength. The larger time constant in the fitting parameters was probably associated with the thermal momentum of the system according to simulations on time dependent surface heating. It is worth noting here, that the simulated increase of surface temperature expected in the experiments was very low and thus the increased current was truly due to the photogeneration.

The power function fit on the photocurrent vs. laser power data gave very similar exponents of ~0.21 for each wavelength. Such a low exponent value implies a complex photogeneration and relaxation mechanism through various trap states in the WS$_2$ nanohybrids. The low exponent is similar to the values obtained for other materials such as graphene (~0.25) [92], ZnO (~0.28) [93], single layer WS$_2$ (0.4) [94] and InSb nanowires (0.2) [95]. The maximum obtained photoresponsivity of ~0.4 A·W$^{-1}$ is excellent considering that it is close to those of
bulk Si based detectors [96] and composites of carbon nanotube and perovskite films [97], and is significantly higher than the earlier reported values for graphene [98, 99] or for most TMDs [100-102]. However it does not compete with CdSe and CdSe/CdS core–shell nanocrystals [103], arrays of ZnO [104] or Si nanowires [105].

Fig. 10. (a) Photocurrent modulation by red laser pulses (λ=661 nm, w0=9 mm 1/e2 beam waist, TEM00, 10 kHz square wave with duration of 50 µs, power of 1, 2, 5, 10, 20, 50 and 100 mW) measured on a serially connected load resistor. (b) Photoresponse to laser pulses (λ=661, 552 and 401 nm denoted as red, green and blue plots) of 20 mW total power corresponding to 29, 52 and 40 nW power on the WS2 nanohybrid considering the 1/e2 beam waists of 9, 7 and 8 mm, respectively (nanohybrid length and diameter of 5 µm and 330 nm, respectively). The time constants correspond to the fitting parameters of bi-exponential growth and decay fitting parameters. (c) Log-log plot of photocurrent vs. total laser power and wavelength, and corresponding power function fittings. (d) Photoresponsivity vs. light power on the nanohybrid.
Table 4. Photoresponsivity Performance parameters [113].

<table>
<thead>
<tr>
<th>Description</th>
<th>Responsivity</th>
<th>Detector type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS nanowire-nanoflake</td>
<td>0.4 AW⁻¹</td>
<td>Photodetector</td>
<td>This work</td>
</tr>
<tr>
<td>Bulk Si</td>
<td>0.1-0.7 AW⁻¹</td>
<td>photodiode</td>
<td>96</td>
</tr>
<tr>
<td>Composites of carbon nanotube and perovskite films</td>
<td>13.8 AW⁻¹</td>
<td>Photodetector</td>
<td>97</td>
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<tr>
<td>Single layer MoS₂</td>
<td>7.5 mA W⁻¹</td>
<td>Phototransistor</td>
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<tr>
<td>Few-Layered WS₂ Films</td>
<td>21.2 μA W⁻¹</td>
<td>Photodetector</td>
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<tr>
<td>ZnO nanowire</td>
<td>4.7 ×10⁴ AW⁻¹</td>
<td>Phototransistor</td>
<td>104</td>
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<tr>
<td>Silicon nanowire</td>
<td>10⁷ A/W</td>
<td>Phototransistor</td>
<td>105</td>
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<tr>
<td>Graphene-metal junction</td>
<td>6.1mA W⁻¹</td>
<td>Photocurrent (PV/PTE)</td>
<td>106</td>
</tr>
<tr>
<td>Graphene p-n junction</td>
<td>10mA W⁻¹</td>
<td>Photocurrent (PTE)</td>
<td>107</td>
</tr>
<tr>
<td>Graphene coupled to waveguide</td>
<td>0.13AW⁻¹</td>
<td>Photocurrent (PV/PTE)</td>
<td>108</td>
</tr>
<tr>
<td>Hybrid graphene-QD</td>
<td>10⁸ AW⁻¹</td>
<td>Phototransistor</td>
<td>109</td>
</tr>
<tr>
<td>Graphene double layer heterostructure</td>
<td>&gt; 1AW⁻¹</td>
<td>Phototransistor</td>
<td>110</td>
</tr>
<tr>
<td>Biased MoS₂</td>
<td>880 AW⁻¹</td>
<td>Photoconductor</td>
<td>111</td>
</tr>
<tr>
<td>WSe₂ p-n junction</td>
<td>16 mA W⁻¹</td>
<td>p-n photodiode</td>
<td>112</td>
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</table>
5 Summary and conclusions

In this thesis a novel WS$_2$ nanowire-nanoflake hybrid nanostructure has been synthesized, characterized and then demonstrated to be a versatile nanomaterial. Treatment of hydrothermally grown WO$_3$ nanowires in the vapor of S at 800°C resulted in the formation of WS$_2$ nanowire-nanoflake hybrids instead of the anticipated WS$_2$ nanowires. The obtained nanostructured material showed p-type semiconducting behavior with a band gap and field effect mobility of 1.4 eV and 0.18 cm$^2$V$^{-1}$s$^{-1}$, respectively. In resistive gas sensors, the WS$_2$ nanohybrid displayed excellent selectivity to H$_2$S (among the tested analytes such as H$_2$S, CO, NH$_3$, H$_2$, and NO) with a high sensitivity of 0.043 ppm$^{-1}$ and a detection limit of 20 ppb. Further, this new nanomaterial also showed high photoresponsivity (0.4 A·W$^{-1}$) in the entire visible spectrum.

Based on these results, it may be concluded that the WS2 nanowire-nanoflake hybrid has a number of fascinating properties making it a versatile nanomaterial similar to other transition metal disulfides and prompting applications in nano and optoelectronics as well as in gas sensing. In a broader perspective, this thesis also sheds light on a potential large-scale synthesis method that may be applied to obtain a large variety of other highly complex nanomaterials by simply doping metal oxide nanostructures in the vapor of S or other chalcogens.
List of references


Original publications


Reprinted with permission from Springer Nature (paper I and paper II)

Original publications are not included in the electronic version of the dissertation.
641. Vuokila, Ari (2017) CFD modeling of auxiliary fuel injections in the blast furnace tuyere-raceway area
642. Vähäsaara, Ilari (2018) Simultaneous localization and mapping using the indoor magnetic field
644. Pramila, Anu (2018) Reading watermarks with a camera phone from printed images
646. Klets, Olesya (2018) Subject-specific finite element modeling of the knee joint to study osteoarthritis development and progression
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Georgies Alene Asres

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF WS₂ NANOWIRE-NANOFILAKE HYBRID NANOSTRUCTURES