Functional nanomaterials of zinc oxide and compounds of vanadium: synthesis and properties

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This thesis includes original results obtained by the author. To the best of my knowledge, it does not contain any data previously published by another person. None of the material included has been submitted for a degree or diploma at any university.

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Abstract

Nanomaterials and, among them, elongated morphologies such as nanowires, nanotubes and nanorods attract a dramatic deal of attention in the current materials research. They are capable of extending functionalities of modern devices and are considered to have exciting applications in a variety of fields including sensors, light- and electron emitting devices, energy conversion and storage, intelligent switches and self-cleaning materials. The ability to produce large quantities of nanomaterials is needed for testing their properties for a broad scope of applications and for the commercialization of emerging technologies. The development of efficient synthesis methods capable of mass production of nanomaterials is becoming crucial.

In this thesis the applicability of ball milling to the efficient production of nanomaterials is assessed. Two key technological materials, ZnO and V₂O₅, are chosen as model systems. ZnO is well known for its semiconducting and piezoelectric properties; it is used in electronics, sensors, light sources and other applications. And V₂O₅ is a widely used material in the field of catalysis and electrochemistry, with applications in electrochromic devices and batteries.

Ball milling of ZnO is found to increase the evaporation ability of the milled material. The effect is not related to the changes in the surface area but attributed to the structural changes in the material. ZnO nanowires are grown by evaporation of the milled powder. Their luminescent spectrum is dominated by a green emission band (at 510 nm) while the near-band-edge emission (at 390 nm) is suppressed.

The unusual morphology of corrugated ZnO nanowires produced by evaporation of the ball milled powder is studied in detail. The nanowires have a hexagonal cross section while their side surfaces are converted into the sequences of predominant \{10\overline{1}1\} and \{10\overline{1}1\} facets. The formation of this unusual morphology is attributed to the presence of stacking faults in nanowires and a high vapor supersaturation.

Ball milling of V₂O₅ powder with a subsequent annealing in a fluidized bed leads to a mass production of nanorods. 1 g of V₂O₅ nanorods is produced in a proof-of-concept test. The formation of nanorods is related to the minimization of surface energy, and surface diffusion plays an important role in the growth mechanism. The beneficial crystal orientation of V₂O₅ nanorods provides an improved cycling
stability for lithium intercalation

The large quantities of $\text{V}_2\text{O}_5$ nanorods produced by ball milling and subsequent annealing in a fluidized bed can be converted to nanorods of other vanadium compounds by simple reduction techniques which preserve the primary morphology. The formation of $\text{VO}_2(\text{B})$, $\text{V}_2\text{O}_3$ and VN phases is achieved by pseudomorphic reduction in vacuum and NH$_3$ atmospheres.

Finally, the electrochemical properties of vanadium nitride for potential applications of this material in supercapacitors are studied. VN possesses capacitive properties in acidic (1M H$_2$SO$_4$), alkaline (1M KOH) and neutral (3M NaCl) electrolytes. The material synthesized by NH$_3$ reduction of $\text{V}_2\text{O}_5$ can retain about 80 % of its capacitance at a high current load of 1 A g$^{-1}$. The cycling stability of VN in 1M H$_2$SO$_4$ and 3M NaCl electrolytes is tested.

Five peer-reviewed journal articles based on the results of the thesis have been published, and one more is currently under preparation.
Journal publications related to this thesis


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Chapter 1

Introduction

1.1 Functional nanomaterials: a brief overview

Functional nanomaterials represent a rapidly growing area of research around the world. The term 'nanomaterials' usually refers to the materials that have at least one dimension smaller than 100 nm [1], although the word is also used occasionally in the literature to describe materials with dimensions below 500 nm. Examples of nanomaterials include nanoparticles (three dimensions are at the nanometric scale) [2], nanowires (two dimensions are suppressed) [3], nanowalls (one dimension is at the scale of nanometers) [4], nanoporous materials [5], nanotubes [6] and many other more complex morphologies. Functional nanomaterials possess new attractive properties - both physical and chemical - due to the combination of their small size and special structural features (such as, for example, crystal orientation, doping, surface functionalities).

Heterogeneous catalysis has probably been the earliest field to benefit from the use of nanomaterials. The application of nanoscale particles as active components of catalysts generally leads to a dramatically increased catalytic activity. Nearly all modern catalysts contain a well-dispersed phase as an active component on a suitable support or within a textural promoter [7]. Alternatively, a solid nanoporous phase presenting a high surface area can be employed [8]. The overall performance of catalytic particles can be further improved if particles with predefined surfaces can be synthesized. For example, Pt nanocrystals with 64% of {100} facets at the surface can significantly outperform conventional Pt catalysts (with uncontrolled surface facets) in the course of NO reduction by CH$_4$ [9]. The composition of the nanoscale particles is also of a high importance. For example, doping of nickel with copper or palladium can greatly enhance the stability of the catalyst during methane decomposition [10,11].

In the last several decades, many other fields of science and technology have ben-
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Effected from the use of nanomaterials including application in sensory devices [12], light and electron emission [13, 14], power sources [15], drug delivery [16], and smart textiles [17]. It is also quite possible that the development of new efficient nanomaterials with tailored structures may provide solutions to the major problems of the current energy crisis such as alternative sources of energy, its storage and conversion [18].

In the case of hydrogen storage the application of nanostructures can efficiently lower the temperatures for the release of hydrogen, or facilitate its diffusion into and out of materials. Nanoporous materials that confine and divide storage media (e.g. \(\text{NH}_3\text{BH}_3\)) in nanosized units can decrease the decomposition temperatures and energy activation barriers for hydrogen release [19]. Core-shell composites can enable fast exchange of protons between the bulk that stores hydrogen and the surface layer designed to make and break \(\text{H}_2\) molecules [18].

Batteries and supercapacitors comprising nanostructured electrodes are capable of having improved energy and power densities due to the larger surface areas, shorter diffusion distances and possible new energy storage mechanisms. A nice illustration of the advantages of nanomaterials for energy storage devices is the recent report on nanowire-based Si electrodes for lithium batteries capable of providing impressive capacities of 4200 mAh g\(^{-1}\) and withstanding 400 % volume changes upon lithium insertion and extraction [20].

1.2 Thesis objectives

A growing number of industrial companies are now seeking to commercialize emerging technologies related to nanostructures. The fundamental problem, however, lies in the scaling-up of materials successfully grown and tested in the laboratory so that they can be produced in bulk and also tested at that level. Only when this is achieved can the hope of efficient commercialization be realized. It follows that the increasing interest in nanomaterials requires a major step to be made towards the development of more efficient methods for their growth. Rapid development of new cost-efficient synthesis techniques for large quantities of nanomaterials is therefore crucial.

In this thesis, the application of mechanical ball milling to the efficient production of nanomaterials is studied. Two key technological materials (ZnO and \(\text{V}_2\text{O}_5\)) are chosen as model systems. ZnO is well known for its semiconducting and piezoelectric properties and for its manifold uses in electronics, sensors, light sources and other applications. \(\text{V}_2\text{O}_5\) (vanadium pentoxide) is a widely used material in the field of catalysis and electrochemistry, with applications in electrochromic devices.
and in batteries. It is demonstrated in the following chapters that ball milling leads to an enhanced evaporation from ZnO vapor sources and formation of unusual corrugated ZnO nanowires. When it is applied to V$_2$O$_5$, the ball milling and annealing approach is capable of making large quantities of V$_2$O$_5$ nanorods with improved lithium intercalation stability.

Compounds of vanadium represent a rich family of compounds including a number of vanadium oxides with different oxidation states of vanadium in them (VO$_2$, V$_2$O$_3$, V$_6$O$_{13}$, etc.), vanadium nitrides and carbides. The production methods for the compounds of vanadium other than V$_2$O$_5$ have generally been less explored than the synthesis techniques for vanadium pentoxide. An attractive way to synthesize these nanomaterials, on the other hand, is to produce them by a direct conversion from the existing nanoscale morphologies of V$_2$O$_5$ itself. The conversion of V$_2$O$_5$ nanoscale morphologies into those of VO$_2$(B), V$_2$O$_3$ and VN is described in this thesis, as well as the study of the end-products themselves. It is shown that the large quantities of V$_2$O$_5$ nanorods produced by the ball milling and annealing approach can be converted into nanorods of these compounds of vanadium.

Properties of the produced nanomaterials are crucial for their anticipated applications, so that some attention is given to this important aspect of research. Specifically, the luminescent properties of ZnO and electrochemical properties of V$_2$O$_5$ and VN are evaluated. The electrochemical tests are focused mainly on vanadium nitride, which has been recently reported as a promising novel material for use in supercapacitors [21].

1.3 Review of related literature

1.3.1 ZnO nanowires

Zinc oxide is a well known and important II-VI semiconductor. It has a direct wide band gap of 3.4 eV and a large excitonic binding energy (60 meV) [22]. This material has a stable wurtzite structure with lattice parameters of $a = 0.325$ nm and $c = 0.521$ nm. The atomic arrangement in ZnO structure can be seen as a system of alternating planes of Zn$^{2+}$ and O$^{2-}$ ions with tetrahedral coordination. Since there is no centre of symmetry there are intrinsic piezoelectric properties. Various nanomaterials of zinc oxide such as nanoparticles [23, 24], nanocrystalline ZnO [25], nanowires [26], nanobelts [27], nanowalls [28], nanotetrapods [29], and nanospings [30] have been produced. By far the greatest attention, however, has been given to ZnO nanowires and a number of exciting applications have been suggested for them.
Nanostructures (and particularly nanowires) have a principal advantage of a large surface area and, as a consequence, a high sensitivity to the specific chemical environment. Their electronic processes are significantly influenced by the surfaces. ZnO nanowire-based sensors, for example, demonstrate high sensitivity even at room temperature [31]. This immediately brings a significant advantage in comparison with more conventional thin film gas sensors which often have to operate at elevated temperatures. A sensitive H₂ sensor (capable of detecting hydrogen concentrations down to 10 ppm in N₂) based on a Pd-decorated ZnO nanorod has been demonstrated [32]. O₂, NO₂ and NH₃ oxidising sensors in a field-effect transistor geometry of single nanowires have also been achieved [33,34].

Prototypes of nanowire light-emitting diodes and lasers have been demonstrated [31]. A hybrid light-emitting p-n junction diode has been produced using ZnO nanorods as n-type material and the hole-conducting polymer poly-2,4-ethylene dioxythiophene/poly(styrenesulfonate) as the corresponding p-type material [35]. A lasing action in nanowires synthesized by both vapor deposition and solution methods has been reported by several groups [36–38]. And Huang et al. observed a threshold of 40 KW cm⁻² under optical excitation in aligned nanowires grown on sapphire substrates [36].

Applications of ZnO nanowires in dye-sensitized solar cells have also been reported [39, 40]. Arrays of ZnO aligned nanowires were grown on the conductive glass substrates and filled with organic material. The use of aligned nanowires as electrodes allows an efficient filling of this layer. The performance of the device based on ZnO nanowires is remarkably better than that of a device based on nanoparticles [41].

ZnO nanowires and nanobelts are likely to become key elements in the emerging area of nanopiezotronics [42]. Wang and coauthors [43,44] showed recently that ZnO nanowires could be a working element in nanogenerators converting mechanic into electric energy. It is a consequence of the dual piezoelectric and semiconductor properties that ZnO nanomaterials can convert their deformation into electric current. This approach is forecasted to be used in implantable power sources compatible with human tissues, such as muscles, and harvesting the mechanical energy needed from the biological environment. In addition to nanogenerators, piezoelectric field-effect transistors, piezoelectric-gated diode and piezoelectric resonators have also been proposed [42].

Several methods for the synthesis of ZnO nanowires have been reported, the most popular being that of vapor phase deposition. In this approach a precursor material is evaporated in the high-temperature zone of a tube furnace and the vapor is transported by a carrier gas or by diffusion to a substrate placed at a lower temperature
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The growth of ZnO nanowires produced in the vapor deposition method is generally described as vapor-solid (VS) or vapor-liquid-solid (VLS) mechanisms. In the VS case, ZnO nanowires form directly from the gas vapor phase by direct condensation [26], and pure ZnO nanowires can be obtained since metal catalysts are not needed. However, the morphology of the final crystals is very sensitive to the growth conditions and in practice some 'catalysts' (in the form of nanoscale particles) have to be used to assist in the formation of the one-dimensional morphology. In such a case it is the VLS process - a different growth mechanism - which controls the growth process. Typically the gaseous reactants from the vapor dissolve into nanosized liquid droplets of a catalyst, and this is followed by nucleation and growth of single crystalline wires through precipitation from the oversaturated solution [45,46]. Au, Cu, Ni and Sn are typical metal catalysts used for the growth of ZnO nanowires. Recently, Pan et al. [47] reported that the growth of ZnO nanowires could also be assisted by Ge particles, the first semiconductor catalyst to be reported. Note that a catalyst can be evaporated together with the source material or pre-patterned on the substrate surface. The equipment required for this method is an atmosphere-controlled tube furnace. The production process is relatively simple, and the cost is low.

Metalorganic chemical vapor deposition (MOCVD) is an alternative method for production of nanowires and nanorods [48], in which a metalorganic precursor decomposes/reacts with oxygen to yield the desired nanorods or nanowires. Two types of precursors are typically used - diethylzinc (Zn(C$_2$H$_5$)$_2$) with an O$_2$/N$_2$O gas mixture, or zinc acetylacetonate hydrate with O$_2$/N$_2$. The advantages of this method include a precise control of nanowire length, a relatively low formation temperature (400 - 700 °C), high efficiency of oriented growth and good compatibility with existing electronic technology. Most products of MOCVD are relatively short oriented nanorods with sharp or flat tips, which can be deposited on various substrates, such as Si, Al$_2$O$_3$, GaAs or fused silica. Production of long nanowires used to be a challenge for the MOCVD method. A recent modification of the growth conditions has led to the production of long nanowires using gold nanoparticles [49]. Because of the sophisticated equipment of the MOCVD reactor, the quantity of the nanowires is low and the cost is high compared with the process of vapor deposition.

A third common method for ZnO nanowire synthesis is the solution process, in which the Zn(NH)$_4^{2+}$ and Zn(OH)$_4^{2-}$ complexes decompose in various solutions [50,51]. Hydrothermal conditions are used in most cases to generate the growth of ZnO nanowires. The advantages of a solution approach are the low growth temperature and perspectives for relatively larger quantity production. To enhance the formation of nanowires and to suppress the formation of other morphologies,
some special strategies are applied in the solution method, including the use of preliminary deposited nanoparticles of ZnO as growth seeds [52], the application of microemulsions [53] and various surfactants [54] to promote 1D growth. When a microemulsion is used, every microemulsion droplet acts as a nanoreactor for the formation of nanoparticles. When different droplets coalesce, nanoparticles can attach to each other by means of an ‘oriented attachment’ mechanism. Cetyltrimethylammonium bromide (CTAB), PVP and polyethylene glycol (PEG) are used as typical surfactants. They can interact with different surfaces of a crystal in a different way, or form rod-like micelles which act as templates for wire growth. By suppressing the growth of some crystal planes, carbamide can lead to the formation of ZnO nanobelts in a solution [55].

The fourth common approach is based on the use of templates with cylindrical channels. The three kinds of templates typically used are anodic alumina membranes, polycarbonate membranes and mesoporous silica. The synthesis of nanowires in these templates is performed by sol-gel or electrochemical deposition methods. The first successful synthesis of ZnO nanowires by sol-gel synthesis inside of a template was performed in 1997 [56]: much earlier than the other methods. However, both electrodeposition and sol-gel processes usually produce only nanowires with a polycrystalline structure instead of the much more desired single-crystalline structures normally produced by other methods. A further drawback is the necessity to dispose of the template after the synthesis. Yet the production of single-crystalline ZnO nanorods by electrodeposition without the use of a template with channels has been recently reported [57, 58].

The issue of achieving large scale synthesis of ZnO nanowires is of central importance. A proper testing of physical properties and proposed applications of nanowires are impossible without the capability to produce material at least in gram, or better, kilogram quantities. The methods described above normally produce only small amounts of samples, typically in the order of milligrams. Ren et al. [59, 60] have reported some minor progress towards the possibility of growth of gram quantities of ZnO nanowires by the vapor deposition method. Evidently the key step lies in the use of porous graphite substrates (such as graphite flakes or carbon cloths) rather than a flat substrate. Such a porous substrate has a relatively large surface area which can greatly enhance the yield of nanowires, and the residual carbon support can be easily burnt away. The fundamental problem of achieving real large scale production up to kilogram levels requires more research and novel approaches and at this time of writing has not been solved.
1.3.2 Nanomaterials of vanadium compounds

Vanadium may exhibit numerous oxidation states, normally between 2+ and 5+ and a rich family of vanadium compounds exists in nature. Particularly, a large number of oxides including VO, VO$_2$, V$_2$O$_3$, V$_2$O$_5$, V$_6$O$_{13}$, V$_4$O$_9$, V$_3$O$_7$ are observed. Other interesting compounds of vanadium are carbides and nitrides, both of which have promising properties for catalysis and electrochemistry. Some brief information about vanadium compounds relevant to the work described in this thesis is given below.

Vanadium pentoxide (V$_2$O$_5$) is an important material in the fields of catalysis and electrochemistry. It is a layered compound belonging to the orthorhombic crystal system with space group D$_{2h}$-P$_{mmn}$ [61, 62]. Three types of oxygen atoms coordinated with one, two and three vanadium atoms, respectively, exist in the lattice. The material structure comprises weakly bonded sheets lying parallel to the (001) crystal plane. The structure of vanadium pentoxide is also characterized by the existence of channels with an effective diameter of 2 Å parallel to the [010] and [001] crystallographic directions. The presence of different types of oxygen atoms and significant anisotropy make the properties of V$_2$O$_5$ structurally sensitive.

A range of applications has been proposed for V$_2$O$_5$ nanomaterials. First of all, V$_2$O$_5$ in nanostructured forms is widely used in catalysis [63]. A widely anticipated application is the use of V$_2$O$_5$ nanomaterials (and especially their elongated structures) in electrodes of Li batteries [64] and electrochromic devices [65]. Kim et al. have demonstrated a field-effect transistor based on individual V$_2$O$_5$ nanofibers [66]. Layers of V$_2$O$_5$ nanowires have been proposed as a material for artificial muscles [67]. V$_2$O$_5$ nanofibers and nanowires can be efficient sensors for ethanol and amines [68,69] and can be used in devices for helium detection [70]. These are only some examples of possible applications of V$_2$O$_5$ nanostructures.

Vanadium dioxide (VO$_2$) is represented by several polymorphs with different crystalline structures [71], the most stable of which is the thermochromic phase of VO$_2$. This material is a rutile structure (denoted VO$_2$(R)) above 68 °C and transforms into a monoclinic structure (VO$_2$(M) which can be described as a slightly distorted rutile structure) below that temperature. The metal-semiconductor phase transition at 68 °C dramatically changes the inherent properties of VO$_2$ [72]. Another commonly observed polymorph of VO$_2$ is the VO$_2$(B) phase with a monoclinic structure derived from V$_2$O$_5$ but with a different valence, equal to 4+, for the vanadium atoms. The stable VO$_2$(R) can be considered as a limit in the so-called Magneli series V$_n$O$_{2n-1}$ of vanadium oxides [73]. These phases contain vanadium in the oxidation state 3+ and an increasing amount of V$^{4+}$ up to VO$_2$. For all members of this series, oxygen octahedra are aligned along two perpendicular directions. It has
been brought forward that VO$_2$(B) can be considered as the limit in the V$_n$O$_{2n+1}$ series (including V$_3$O$_7$, V$_4$O$_9$ and V$_6$O$_{13}$) [74]. These phases contain vanadium in the oxidation state 5+ and an increasing amount of V$^{4+}$.

The thermochromic phase of VO$_2$ is thought to be an excellent candidate for applications to smart windows in which the environmental heat flow into buildings is controlled [75]. Such windows conveniently permit penetration of both heat (infrared radiation) and visible light at a low temperature, whilst only visible light is transmitted above a certain critical temperature. Such an environmentally-friendly technology promises a drop in energy consumption in offices and homes in the summer seasons by reducing the need for conventional air conditioning. The important point here is that the critical phase transition temperature of VO$_2$ (68 °C) is close to practical temperatures. Moreover, the phase transition temperature can be shifted close to room temperature if a nanocrystalline [76] or W-doped [77] VO$_2$ material is used. There are other applications based on the phase transition for the thermochromic phase of VO$_2$ including switching elements and dedicated detectors generally.

The VO$_2$(B) phase has also been considered for a number of applications including its use in lithium batteries with aqueous [78] and nonaqueous electrolytes [79]. Nanocrystalline VO$_2$(B) derived from vanadium oxide aerogels showed specific capacities for lithium as high as 500 mAh g$^{-1}$, and the stable electrochemical response was achieved upon cycling between 4 and 2.4 V vs Li$^+$/Li [80]. Elsewhere a high reversible capacity of above 300 mAh g$^{-1}$ was observed for VO$_2$(B) at a voltage window of 3.5 - 1 V and a moderate reversible capacity of about 200 mAh g$^{-1}$ was achieved at 3.5 - 2 V [81]. Liu et al. [82] have reported a reversible photoswitching behavior in VO$_2$(B) nanobelts. Their conductance increased two- to threefold when they were exposed to infrared radiation.

Vanadium trioxide (V$_2$O$_3$, also commonly referred to as vanadium sesquioxide) is a compound with an α-corundum structure [83]. This material possesses a first-order phase transition from the metallic paramagnetic (PM) state to a low-temperature antiferromagnetic insulating (AFI) state with a monoclinic structure at about 150 K [72]. Various low-temperature switching devices based on this phase transition can be realized. V$_2$O$_3$ powders are used in catalysis [84] and conductive polymer composites [85]. V$_2$O$_3$ has also been reported to exhibit the properties of a heat mirror - implying an unintelligent version of a VO$_2$ coating [86].

Vanadium nitride (VN) has a simple cubic NaCl structure with both high thermal and electrical conductivities, and also the attractive features of chemical and thermal stability. Well-known for its wear resistance and extreme hardness it also resists chemical attacks of most solvents, with the exception of hydrofluoric acid [87].
Vanadium nitride is reported to exhibit superconductive properties below the reported critical temperature of 9 K (see, for example, [88]). Suggested applications of VN include solar control coatings [89], lubricants [90], barrier coatings for microelectronic devices [87], and catalysts [91]. More recently attractive capacitive properties have been reported for this remarkable compound, pointing up potential applications in electrochemical supercapacitors [21,92].

The synthesis of $\text{V}_2\text{O}_5$ nanomaterials has been researched much more than the preparation of other compounds of vanadium, and mostly chemical methods have been employed for making $\text{V}_2\text{O}_5$ nanostructures. More particularly it is sol-gel processing which has been traditionally considered as the method of choice for preparing $\text{V}_2\text{O}_5$ nanostructures. Two main techniques have been developed for preparing $\text{V}_2\text{O}_5$ gels: (1) acidification of $\text{NaVO}_3$ using an ion-exchange process and polymerization of the resultant $\text{HVO}_3$ in water [93, 94], and (2) hydrolysis and condensation of vanadium alkoxide [95]. The gels obtained are represented as a hydrated vanadium pentoxide with the composition $\text{V}_2\text{O}_5\cdot n\text{H}_2\text{O}$. The orthorhombic phase of crystalline $\text{V}_2\text{O}_5$ is usually obtained by heating vanadium pentoxide gels above 350 °C in air.

Membranes with cylindrical pores (for example, membranes of anodic alumina) are used for preparing arrays of $\text{V}_2\text{O}_5$ nanowires by either sol-gel [96] or electrodeposition [97] methods. Hydrothermal syntheses are also commonly employed procedures for preparing nanostructures of $\text{V}_2\text{O}_5$ [98]. Nanobelts of $\text{V}_2\text{O}_5$ have recently been synthesized by thermal evaporation [99].

Nanomaterials of $\text{VO}_2$(B) have been synthesized mainly by hydrothermal reduction. For example, Tsang et al. have synthesized nanocrystalline $\text{VO}_2$(B) through the reduction of an aqueous $\text{K}_3\text{VO}_4$ solution with potassium borohydride at pH equal to 4 [100]. $\text{VO}_2$(B) nanowires have been obtained by ethylene glycol reduction of $\text{V}_2\text{O}_5$ [101]. And nanobelts of $\text{VO}_2$(B) have been obtained hydrothermally from aqueous solutions of ammonium metavanadate and formic acid [82]. Li et al. have produced nanorods of $\text{VO}_2$(B) by a hydrothermal treatment of $\text{V}_2\text{O}_5$ with formaldehyde [102]. Nanotextured $\text{VO}_2$(B) have been obtained by a quite different approach involving the vacuum annealing of $\text{V}_2\text{O}_5$ aerogels [103].

Although the synthesis of thin films of thermochromic $\text{VO}_2$ have achieved significant attention, there is a limited number of reports as to the synthesis of distinct morphologies of $\text{VO}_2$ nanomaterials. The synthesis of nanomaterials of the thermochromic phase of $\text{VO}_2$ can be achieved through the annealing of nanoscale morphologies of $\text{VO}_2$(B), which tend to recrystallize into the stable rutile phase when annealed in inert gases. For example, $\text{VO}_2$(B) nanobelts were transformed to those of $\text{VO}_2$(R) by annealing in Ar at 500 °C [104]. Thermochromic nanorods of $\text{VO}_2$ were prepared by heating $\text{VO}_2$(B) nanorods in N$_2$ atmosphere up to 700 °C at a
heating rate of 10 °C min\(^{-1}\) [105]. Another possible method is physical vapor deposition in vacuum. Guiton et al. [106] and Sohn et al. [107] have produced nanowires by these means. In the latter work oriented nanowires of VO\(_2\) were produced by using single-crystalline sapphire substrates [107].

Nanostructured V\(_2\)O\(_3\) has been synthesized by chemical methods. V\(_2\)O\(_3\) nanocrystals have been prepared by the decomposition of NH\(_4\)VO\(_3\), followed by nitridation in an autoclave with a metallic Na flux at 450 - 500 °C [108]. Powders and films of V\(_2\)O\(_3\) have been prepared by the hydrogen reduction of sol-gel synthesized V\(_2\)O\(_5\) at above 500 °C [109]. V\(_2\)O\(_3\) nanopowder with spherical particles has been produced by a reducing pyrolysis of (NH\(_4\))\(_5\)[(VO)\(_6\)(CO\(_3\))\(_4\)(OH)\(_9\)]\(\cdot\)10H\(_2\)O in H\(_2\) [110].

Conventionally, vanadium nitride is prepared by the direct nitridation of vanadium in N\(_2\) or NH\(_3\) atmospheres at 1000 K [87]. A number of strategies leading to VN nanostructures have been reported. Decomposition of gas-phase starting materials by an atmospheric microwave plasma-torch leads to the formation of nanoparticles with sizes of 10 - 25 nm [111]. Nanostructured VN can be obtained by a direct liquid-solid reaction between VCl\(_4\) and NaN\(_3\) at 600 °C [112]. Nanoparticles and hollow sphere morphologies have been achieved by reacting VCl\(_4\) and NaNH\(_2\) [113]. Other methods include the carbothermal reduction of vanadium pentoxide in N\(_2\) at about 1500 °C [114], the electrochemical method [115] and the reduction-nitridation reaction between VCl\(_4\), NH\(_4\)Cl, and Mg [116].

The large scale production of V\(_2\)O\(_5\) nanomaterials and convenient methods of converting them into nanomaterials of other vanadium compounds (including VO\(_2\)(B), V\(_2\)O\(_3\) and VN) is described in chapters 5 and 6.

### 1.3.3 Ball milling and annealing synthesis method

A promising way to produce large amounts of elongated nanomaterials (nanotubes, nanorods and nanowires), including those related to energy storage in batteries and supercapacitors is the ball milling and annealing method. Large quantities of BN nanotubes [117] and C\(_3\)N\(_4\) nanorods [118] have recently been produced in this way. It is possible that the method can be modified to yield large quantities of nanowires of other materials, including zinc oxide and vanadium oxides and compounds.

The two-step process consisting of ball milling and subsequent annealing, first developed in 1999 for the synthesis of C and BN nanotubes [119,120], has been shown recently to be an efficient way to enhance the growth of other one-dimensional nanostructures. The first step in this method is a mechanical treatment of a precursor powder or/and synthesis through a mechano-chemical reaction. The obtained product can be annealed at an elevated temperature to yield the desired product. Such a method can be potentially applied to the growth of large quantities of nanowires
and nanorods of various materials.

Mechanical treatment in ball mills is well known as an efficient way for the synthesis of various metastable phases (including high temperature and high pressure ones) and induction of solid-solid, solid-liquid and solid-gas chemical reactions normally excluded at room temperature. Mechanical milling typically leads to a decrease of crystallite size, a greater increase of the surface area of powders, the changes in chemical reactivity and volatility of the materials and highly homogeneous mixing of components. The appearance of contaminations in the form of small metal particles from the container and ball materials is not always a drawback and can be beneficial for some particular syntheses.

The effects provided by ball milling have been proved to be helpful for the synthesis of one-dimensional nanostructures. Nanowires and nanorods of ZnO, SnO$_2$, Ga$_2$O$_3$, GaN, AlN, GaP, C$_3$N$_4$, SiC, HfB$_2$, ZrB$_2$ and CdSe and nanotubes of BN and SnO$_2$ have been synthesized by annealing of the corresponding pre-milled powders [121–131]. Despite of the large variety of materials obtained, the important effect of ball milling and its intrinsic mechanisms have not been carefully investigated.

Briefly, as a result of mechanical milling, the milled powders have smaller particle sizes and higher surface areas. This usually leads to improved volatility and chemical reactivity in comparison with original commercially available powders. The effect of the higher volatility induced by ball milling can be used to grow nanowires by vapor deposition at lower temperatures. As a consequence of modified volatility, nanowires can also be successfully grown under conditions at which the formation of nanowires is normally impossible. Nanowires of ZnO, SnO$_2$, Ga$_2$O$_3$, GaN and GaP, for example, have been successfully grown from the ball-milled powders [121–125]. Ball milling treatment helps the formation of single-crystalline nanowires. For example, only polycrystalline curled GaP nanowires or ZnO plate-shaped chips were obtained by vapor deposition of unmilled GaP and ZnO powders [121,127], while high-quality single-crystalline nanowires or nanobelts were grown from milled powders under the same synthesis conditions. Ga$_2$O$_3$ nanobelts [125] and GaN nanoribbon rings [126] were obtained from milled GaN samples evaporated at 930 - 940 °C. In contrast, no 1D nanostructures were grown from unmilled samples due to insufficient vaporization of the primary GaN powder. The evidence for an enhancement of the growth of one-dimensional nanostructures due to preliminary ball milling is obvious.

The smaller size, higher surface area and new metastable structure of milled powders also lead to higher chemical reactivities. In some cases, high chemical reactivity is further increased by a large number of structural defects induced by ball-milling. SiC nanowires and nanowire networks were produced by Li et al. [128]
from ball-milled powders in a graphite reaction cell. The mixture of milled Si and SiO$_2$ powders was used as a precursor material to generate SiO vapor, which was an essential step for the synthesis. A preliminary ball milling treatment appears to be a key factor since no nanowires grew out without it. This effect was attributed to an enhanced chemical reactivity [128].

Various metastable phases can be produced via structural disordering and mechanochemistry during the ball milling process. These phases possess excessive intrinsic energy, and they tend to recrystallize at moderate temperatures to yield thermodynamically stable products. This crystallization behavior can be controlled by a variation of the annealing conditions and may lead, at least for some materials, to 1D morphology. Such solid-state transformation of a metastable milled precursor was found to occur for BN nanotubes [117] and C$_3$N$_4$ nanorods [118].

BN nanotubes were synthesized in large quantities (up to 1 kg) by Chen et al. [117]. The initial precursor was a mechanically disordered nanoporous BN or nitrogen-containing B powder produced by the mechanical treatment of boron powder in an atmosphere of ammonia. Such amorphous powders are metastable and undergo solid-state crystallization upon annealing conditions. Some nanotubes can grow catalytically on tiny metal particles which are milling contaminants. Such syntheses are based, therefore, on the combination of two effects provided by ball milling, namely metastability of preliminary products and homogeneous introduction of small metal particles which can act as catalysts for heterogeneous growth. Carbon nanotubes were grown in the same way [120].

In other work a carbon nitride precursor for the synthesis of C$_3$N$_4$ nanorods was produced by a mechano-chemical reaction between ammonia and mechanically disordered carbon powder [118]. The material obtained was metastable and crystallized into nanorods during the annealing in NH$_3$ atmosphere. The rod-like hexagonal morphology of C$_3$N$_4$ was explained by the "lowest surface energy" arguments. The growth rate of [001] direction was found to be more than twice as fast as those of other directions, and stacking along the [001] direction was considered to be energetically favorable.

The effects of mechanical treatment favoring the formation of nanowires are not clearly defined in some cases. However, if ball milling obviously helps the growth of nanowires, it might be attributed to combined effects of various phenomena induced by the mechanical treatment. For example, milling of a HfCl$_4$/B mixture was found to be beneficial for the formation of HfB$_2$ nanorods [129]. In this case annealing of unmilled samples also leads to the formation of HfB$_2$ rods but with a lower yield and a wider diameter distribution. The positive influence of ball milling in this work might be attributed to a combination of an excellent mixing of components, the
increase of surface areas of powders, mechano-chemical reactions and the presence of contaminating Fe nanoparticles.

Finally, it is to be noted that micro- and nanoneedles of CdSe and micro- and nanotubes of SnO$_2$ have been produced by Piqueras et al. [130,131] by evaporation of compacted milled and unmilled powders on the surface of compacted disks. Micro- and nanostructures were grown both from unmilled and milled samples but the amount of 1D structures is higher and their morphology is more homogeneous in the case when mechanical milling is used. The positive influence of mechanical treatment can be attributed to a combination of a higher volatility and an increase in the number of defects and small crystals with orientations favorable for the growth of 1D structures.

It can be concluded from this large body of evidence that the combination of mechanical milling with subsequent annealing can be applied for the production of large quantities of 1D nanostructures. This has been already achieved for BN nanotubes and C$_3$N$_4$ nanorods by the solid state transformation of milled powders into one-dimensional structures. This suggests that the large scale approaches including a ball-milling step can be extended and modified for the production of nanowires and related nanomaterials of other systems.

1.4 Thesis structure

This thesis is organized into eight chapters. Chapter 1 (above) comprises a literature review and outlines thesis objectives. Chapter 2 introduces experimental techniques used in this study, including synthesis approaches, characterization techniques and electrochemical testing procedures. The influence of ball milling on the evaporation ability of zinc oxide and its application to the growth of ZnO nanowires is covered in Chapter 3. The unusual corrugated morphology of the nanowires obtained from milled ZnO powder is discussed in Chapter 4. Chapter 5 studies large quantity production of V$_2$O$_5$ nanorods by a combination of mechanical milling and annealing in a fluidized bed. The assessment of electrochemical properties of nanorods is also included in this chapter. Chapter 6 describes the conversion of V$_2$O$_5$ nanomaterials into those of a number of other compounds of vanadium (particularly, VO$_2$(B), V$_2$O$_3$ and VN) by reduction techniques involving the conservation of morphology. Chapter 7 presents capacitive behavior of vanadium nitride in various aqueous electrolytes. Finally, Chapter 8 is a summary of the results including comments on promising directions for future research.
Chapter 2

Experimental techniques

This chapter gives a brief overview of the experimental techniques used for preparation of nanomaterials, their characterization and testing. Most of the experimental approaches are quite complex and/or involve sophisticated equipment. Therefore, only main features and capabilities of each technique are introduced. Detailed descriptions can be found in textbooks and monographs.

2.1 Synthesis techniques

2.1.1 Ball milling

Most of the presented synthesis routines involve ball milling as an important step. Ball milling is a material processing technique based on modification of materials by subjecting them to impacts of balls. Typically, a certain amount of a powder sample is loaded into a milling vial and is processed by impacts of balls and by rubbing of balls against each other and the vial’s wall. Conventionally, the technique has been used for decreasing the particle size in materials and grinding large pieces of rocks. Following the advancement of this technology, more sophisticated ball milling machines capable of accelerating balls up to high speeds have been created. High-energy ball milling that is achieved by grinding with balls of large kinetic energy appears to be capable of structural modification and creating a number of interesting phases. A list of special phases achieved by ball milling includes nanocrystalline materials, quasi-crystals, supersaturated solutions and some other non-equilibrium materials. In addition, ball milling technique is capable of inducing chemical reactions that do not normally happen at room temperature (the phenomenon referred generally to as mechanochemistry or reactive ball milling). A more detailed overview of the ball milling technique can be found in several monographs, e.g. in [132].
A number of ball milling devices (shaker mills, attritors, planetary ball mills, and vibratory ball mills) have been designed for processing powders inducing structural transformations and new phases. A magneto-ball mill (also known as Uni Ball Mill or vertical planetary ball mill) [133, 134] has been used in the current study. The schematic drawing of the ball mill is shown in Figure 2.1. A cylindrical milling vial (with a volume of about 300 ml) rotates around a horizontal axis at rotation speeds in the typical range of 100 - 200 rpm and four grinding balls (25.4 mm in diameter) are placed inside of it. An external magnet is located outside of the milling container. Affected by the gravitation force and the magnetic field created by the magnet, balls are elevated to the top of the vial and fall down creating an impact. The milling mode (ball movement pattern) can be adjusted by changing the speed of rotation and the position of the magnet. The milling vial is sealed with an O-ring and a valve in the operation mode and can be filled with a gas of choice prior to the start of milling.

2.1.2 Thermal annealing

The annealing/evaporation experiments were conducted in conventional horizontal tube furnaces. Such a furnace represents a box thermally insulated from the environment that has an opening for the insertion of a quartz or alumina tube. The material sample can be placed inside of the tube where high temperatures (up to 1500 °C) can be created by heating elements. One end of the tube is connected to the gas supply pipeline while another end is connected to the vent. The flow of a
Figure 2.2: Two types of annealing experiments: static annealing (a) and thermal evaporation and vapor deposition (b).

particular gas (Ar, O₂, etc.) can be established in the tube in this way.

The tube furnaces were used for annealing of powders and for evaporation experiments. In the former case, the combustion boat with the material of interest in it was placed in the tube and the desired gas was passing over the sample. If air atmosphere was required, the ends of the tube were left opened to the environment during heating. In the evaporation experiments, some Si substrates were placed downstream and the inert carrier gas (Ar) was used to carry vapors from the initial powder (about 300 mg in a combustion boat) located in the hot zone of the furnace to substrates located in the cooler zones. The schematic drawing of two types of experiments is shown in Figure 2.2.

Some of the furnaces can also be used for temperature-programmed experiments (where temperature is increased at a fixed rate) if the temperature control in the furnace is designed well for that purpose. The temperature-programmed annealing has been applied to preparation of vanadium nitrides and is described in Chapter 6.

Three different tube furnaces have been used in the current study: Carbolite CFM 14/2 (Sheffield, England), Lindberg/Blue M STF 54233C (USA) and a double-zone furnace (Jetlow furnaces, Melbourne, Australia). They differ in tube diameter, quality of temperature control, ability to use particular gases that can be connected in the laboratory. Each of the following chapters specifies which furnace was used in the corresponding experimental section.


2.2 Characterization techniques

2.2.1 X-ray powder diffraction

X-ray diffraction (XRD) technique is used as a primary approach for characterization of phases of materials. The technique allows an operator to identify crystalline compounds by means of their peak positions in a diffraction pattern. When a crystalline material interacts with X-rays, the X-rays get diffracted if the Bragg condition

$$n\lambda = 2dsin\theta,$$

is satisfied, where n denotes an integer, \( \lambda \) is the wavelength of X-ray, d is a lattice spacing in the material and \( \theta \) is the angle between the beam and the lattice plane.

Lattice distances can be calculated from the diffraction pattern. Broadening of X-ray reflections can be used for estimation of grain (crystallite) size. The XRD measurement was performed in this study using Philips analytical X-ray spectrometer with Co radiation (\( \lambda = 0.1789 \) nm) and 2\( \theta \) Bragg-Brentano geometry. The XRD technique is covered in detail in specialized textbooks (e.g. [135,136]).

2.2.2 Scanning electron microscopy

Scanning electron microscopy (SEM) is a key tool in this study to assess the morphology of nanomaterials. In order to take an image of a sample, a converged beam of electrons accelerated by a voltage of 3 - 20 kV is scanned across the sample. The interaction of the beam with the sample induces lower energy secondary electrons to escape from the subsurface regions of the sample. By detecting the presence and amount of secondary electrons at different spots in the sample it is possible to obtain realistically looking 3D-like images of the surface topography. The secondary-electron imaging is a primary technique used for the estimation of samples’ morphology in materials science and related studies in physics or chemistry [137].

A number of other useful signals can be obtained and detected in a scanning electron microscope. These signals include backscattered electrons, characteristic X-rays and light (cathodoluminescence). Specifically, cathodoluminescence (CL) is an important tool to assess optical properties of semiconductor nanomaterials and their electronic properties (e.g., detect the presence of defects). When the sample is irradiated by a beam of electrons, their interaction with the sample excites the native electrons to the conduction band. The excited electrons tend to recombine with holes, producing photons with energies equal to the difference in energy between the excited and recombined states. The information is useful for evaluation of light
emission properties of materials and consistent with band structures and defect levels in materials.

Field-emission scanning electron microscope Hitachi S-4500 was used in the present study to assess the morphology of nanomaterials.

### 2.2.3 Transmission electron microscopy

Transmission electron microscopy (TEM) is an efficient tool to study the structure of nanomaterials and obtain crystallographic information about them. This technique is based on the interaction of high energy (200 - 300 keV) electron beam with a material. The intensities of the direct and diffracted electron beams after the sample are analyzed and useful diffraction patterns and various types of images (bright-field, dark-field and high resolution images) can be obtained. An introductory overview of transmission electron microscopy is well given in [138].

When electron beam passes through a crystalline sample, it gets partially diffracted, and the corresponding diffraction pattern consisting of a direct 000 beam and various diffracted hkl beams focused into spots (for crystalline samples) is formed in the back focal plane of a TEM instrument. By choosing a corresponding mode of operation of the microscope, diffraction pattern can be visualized on the screen or on the film. The dotted electron diffraction pattern is typical for single crystals or samples consisting locally of a small number of crystallites. If a polycrystalline material is studied, the diffraction pattern represents a system of rings while the diffraction pattern of an amorphous or nearly amorphous material includes strongly broadened rings. A particular part of a sample can be selected by choosing it with a special aperture and crystallographic information such as lattice distances, orientation of the sample, preferential directions of elongation, faceting, etc. can be deducted.

In order to form bright-field or dark-field images in a transmission electron microscope, only one of the diffracted beams is used. It can be selected using an aperture by shifting it to a corresponding diffraction spot or tilting the electron beam so that the required beam is not blocked by the aperture. The direct 000 beam is used to form bright-field images (which is the most common imaging mode in TEM) and other beams can be selected to form a dark-field TEM image. The latter mode can be useful, for example, when one wants to evaluate directly the grain size in polycrystalline materials or detect twins and texture in the sample.

Figure 2.3 shows an example of a selected area diffraction pattern, bright- and dark-field images of a polycrystalline aggregate of vanadium nitride nanoparticles. The diffraction pattern has a typical appearance of that for a polycrystalline material, showing a sequence of rings at various distances. The intensity of the rings is not
homogeneous and some brighter arcs can be visible, while the rest of the circle is not pronounced. Such an effect comes from the texture (i.e., a preferential orientation of grains) in the sample. The intense spot in the middle of the pattern corresponds to the direct electron beam. A bright-field image (which is formed by using the direct beam) is shown in figure 2.3b. When a diffracted electron beam (shown with a circle in the diffraction pattern) is chosen, the dark-field image (Figure 2.3c) forms.

High resolution imaging mode reveals the lattice planes of crystalline materials. In order to perform this kind of imaging, no aperture (or very wide aperture centered around the direct beam) is used. The image is formed by interference of various beams passed through the sample. If the position of the sample is appropriate (i.e., some lattice planes are located approximately parallel to the electron beam) the lattice planes can be visualized as black or white lines (the position depends on focusing conditions). If more than one set of planes is parallel to the beam, two-dimensional lattice images can be obtained and rows of lattice points can be directly observed. Figure 2.4 shows a high resolution image of a vanadium oxide nanocrystal.

Phillips CM300 transmission electron microscope was used in the current study. The samples were prepared by placing ethanol droplets onto carbon-coated TEM copper grids and dispersing small amounts of materials in the solvent.

2.2.4 X-ray energy-dispersive spectroscopy

X-ray energy dispersive spectroscopy (XEDS) is a technique used for element composition analysis in electron microscopes. High-energy electrons hit the sample and interact with inner-shell (core) electrons of atoms. If enough energy is transferred, the electrons escape from the attractive field of nuclei, leaving holes in inner shells. In order to minimize the energy of the ionized atoms, the electrons from outer
shells undergo a transition to unoccupied energy states in the inner shell of the corresponding atoms, releasing characteristic X-ray photons. Each element releases X-rays with particular energies (wavelengths) and, therefore, this effect can be used for identification of elemental composition of the samples.

In this study, we used XEDS both in transmission and scanning electron microscopes for qualitative estimation of materials' composition. When quantitative composition determination was necessary, the scanning electron microscopy (JEOL JSM6400) was used.

2.2.5 Electron spin resonance

Electron spin resonance (ESR) is a technique convenient to detect effects related to the presence of unpaired electrons. The sample is placed in the constant magnetic field that induces splitting of the electronic energy levels of unpaired electrons or radicals. The energy levels with lower energies are normally occupied. When an alternating magnetic field with varied frequency is switched on, the signal related to inter-level transitions is detected at the appropriate frequency. The position of the signal may shift or obtain fine structural features depending on the local environment in the material.

In this study, ESR was used to evaluate the presence and quantity of $V^{4+}$ ions in $V_2O_5$, i.e. evaluate the degree of reduction of this material since stoichiometric $V_2O_5$ is ESR-silent. JEOL JES-PE ESR spectrometer was used for collecting the spectrum.
2.2.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a spectroscopic technique that measures the elemental composition at the surface of materials and chemical state of the detected elements. XPS spectra are obtained by irradiating a material with a beam of aluminum or magnesium X-rays and measuring the kinetic energy and number of electrons that escape from the surface layer (several nanometers in depth) of the material being analyzed. XPS requires ultra-high vacuum conditions for measurements.

The XPS spectra are usually plotted as the intensity of the measured signal versus binding energy of electrons. Binding energy is characteristic of particular elements and can be calculated from the energy of X-rays and kinetic energy of electrons escaping from the sample. XPS detects all elements with an atomic number of 3 and above (i.e. the technique cannot detect hydrogen and helium). The position of a certain element's peak depends also on the chemical state of the element (e.g., its oxidation state).

The XPS measurements were performed on ESCALAB220i-XL (VG Scientific, UK) instrument using Al Kα excitation source. The high-resolution spectra were collected with 20 eV pass energy. The peak fitting was performed using free XPS-Peak 4.1 software.

2.2.7 Low-temperature N₂ sorption

Nitrogen sorption (both adsorption and desorption) at the clean surface of dry solid powders is the most common method for determining the surface area of these powders as well as the pore size distribution of porous materials. Prior to a gas sorption experiment, the material is heated and degassed in vacuum to remove adsorbed foreign molecules. The sample is then placed into an evacuated test tube at the temperature of liquid nitrogen (-195.6 °C), and controlled doses of N₂ gas are introduced. As a result, the certain amount of gas is adsorbed. Alternatively, controlled doses of N₂ can be withdrawn, leading to the desorption of the gas. The amounts of gas molecules adsorbed or desorbed are determined by the pressure variations due to the adsorption or desorption by the material. Knowing the area occupied by one adsorbate molecule and using an adsorption model, the total surface area of the material can be determined. Brunauer-Emmett-Teller (BET) model of multilayer adsorption [139] is used in most cases for calculating the surface area.

The specific surface area that can be determined by N₂ sorption ranges from 0.01 to over 2000 m² g⁻¹. The pore size distributions can also be determined from the adsorption/desorption isotherms. The range of pore sizes that can be measured is
from a few Å up to about half a micron.

Micromeritics Gemini V series surface area analyzer and Quantachrome instruments Quadrasorb SI were used in this work to measure the specific surface areas and pore size distributions.

2.3 Electrochemical testing techniques

Two electrochemical techniques, cyclic voltammetry and galvanostatic charge/discharge, were applied to test electrochemical properties of V$_2$O$_5$ nanorods and VN nanomaterials in this study.

![Graphs of electrochemical characterization](image)

Figure 2.5: Electrochemical characterization of a commercially available V$_2$O$_5$ powder (Sigma-Aldrich) in 3M NaCl electrolyte. (a, b) Applied potential versus time in a cyclic voltammetry experiment and the corresponding CV curve at the sweep rate of 1 mV s$^{-1}$. (c, d) Applied current versus time in a galvanostatic charge/discharge experiment and the corresponding GC curve at the current density of 50 mA g$^{-1}$. 
2.3.1 Cyclic voltammetry

In cycling voltammetry (CV) experiments, a three-electrode cell is connected to a potentiostat, and the potential of the working electrode (versus reference electrode) is increased and decreased at a desired sweep rate. The measured signal is the current between working and counter electrodes. The shape of the applied potential versus time and a CV curve for a commercially available V$_2$O$_5$ powder is given in Fig. 2.5a,b. This is an example of a material with capacitive properties. The CV curve of such a material represents a box (ideal capacitive behavior) or a similar shape. The CV technique is very useful for the estimation of capacitive properties of materials and studying redox surface reactions that can be resolved as peaks in a CV profile. Capacitances can be estimated from the area enclosed by a CV curve.

2.3.2 Galvanostatic charge/discharge

In galvanostatic charge/discharge (GC) experiments, the working battery or capacitor electrode is charged and discharged at a fixed value of current (flowing between working and counter electrodes) controlled by a galvanostat. The potential of working electrode versus reference electrode is a measured value. Figure 2.5c,d shows the shape of applied current versus time and a typical charge/discharge profile of the material with capacitive properties (commercially available V$_2$O$_5$ powder in this example). The shape of such profile is close to triangular and the capacitance can be evaluated (from charge or discharge branch) according to the formula

\[ C \ (\text{F/g}) = \frac{I \ t}{V}, \]

where \( I \) is the current density (per gram of material), \( t \) is the time of charging/discharging and \( V \) is a potential window.

In the current study, all capacitances (Chapter 7) were estimated from the discharge branch. Charge/discharge capacities of electrodes in lithium batteries (Chapter 5) can be calculated as the total charge (integrated current) entering or leaving the electrode. Further information on electrochemical techniques and their applications to materials for supercapacitors and batteries can be found elsewhere [140,141].
Chapter 3

Ball milling of ZnO and preparation of nanowires

3.1 Introduction

As it was discussed in Chapter 1, a number of authors reported that the use of ball milled powders as vapor sources in the thermal evaporation approach led to an enhanced growth of nanowires [122,127,142,143]. In some cases, nanowires and nanobelts could be grown under conditions where the growth of these nanostructures is not normally accessible. For example, only polycrystalline curled GaP nanowires were obtained by vapor transport of unmilled GaP powders [127], whereas high-quality single-crystalline nanowires were grown from milled powders under the same synthesis conditions. Ga$_2$O$_3$ nanobelts [125] and GaN nanoribbon rings [126] were obtained from milled GaN samples evaporated at 930 - 940 °C. In contrast, no 1D nanostructures were grown from unmilled samples and this was explained by the insufficient evaporation ability of the initial GaN powder.

Although the enhanced growth of nanowires from milled powders has been reported, the attention in previous publications was mainly focused on the characterization of the nanomaterials. The authors assumed that milling led to stronger evaporation, which was responsible for the observed effects, but the evaporation behavior of the milled materials was not studied in detail. No measurements of the amount of vapor generated under annealing were presented in those papers. The influence of the milling mode was not investigated either. However, detailed knowledge about the evaporation of milled materials is important for their successful application as vapor sources since many nanomaterials are produced by thermal evaporation method. Therefore, further investigation is needed. Ball milling effects can be related not only to the changes in surface area but also to structural changes in the milled materials.
Chapter 3. Ball milling of ZnO and preparation of nanowires

In this chapter, the effects of ball milling on the evaporation behavior of ZnO powder and the production of ZnO nanowires by evaporation of the milled powder are studied. The significant changes in the evaporation behavior of the milled sample are detected. The contribution of surface area and defects to the enhanced evaporation of the milled material is discussed. The influence of milling mode (high-energy or low-energy milling conditions) is also considered. The morphologies and luminescent properties of ZnO nanowires produced by evaporation of the ball milled vapor source are analysed.

3.2 Experimental

A steel magneto-ball mill was used for ball milling treatment. Two modes of milling were used to treat ZnO powders. Under high-energy milling conditions, the balls were elevated by a rotating cell and a magnetic field to the top of the vial and fell down creating a strong impact with powder at the bottom surface of the vial. In this mode of operation, the magnet was located at the bottom of the mill at a 45° position in relation to the vertical direction. The mill was rotating around a horizontal axis at the speed of 160 rpm. Under low-energy conditions, the magnet was removed and no magnetic field was present. The balls were rolling at the bottom of the vial and the powder was processed by friction mainly. Rare weak impacts were observed from time to time. In each procedure, 3 g of a commercial ZnO powder (Ajax Chemicals, 99.5 % purity) were placed in the vial and the milling was performed for 100 h in nitrogen atmosphere (excessive gas pressure of 100 kPa) at room temperature.

The evaporation behavior of samples was studied in a conventional tube furnace (Carbolite CFM 14/2, Sheffield, England). Unmilled ZnO material as well as ZnO powders milled under high-energy and low-energy conditions were heated at 1300 °C in Ar flow (0.4 l min\(^{-1}\)) for various periods of time. The standard amount of powder (300 mg) was used in each experiment and loaded into a combustion boat and the weight loss was measured afterwards.

ZnO powder milled under high-energy conditions was used to grow ZnO nanowires by a thermal evaporation process. The growth of nanostructures was conducted in the same tube furnace. The vapor source (milled powder) was placed at the centre of the furnace at around 1300 °C. Ar gas flow (0.4 l min\(^{-1}\)) was used as a carrier gas to transfer ZnO vapor from the hot zone to a cooler zone of the furnace for deposition. Several Si substrates (N-type, (100) surface orientation) were located downstream and used for vapor deposition in a lower temperature zone.
Milled ZnO powders and as-grown products of vapor deposition were comprehensively characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) equipped with x-ray energy-dispersive spectroscopy (XEDS), cathodoluminescence (CL) spectroscopy and transmission electron microscopy (TEM). The surface area of both the milled and unmilled ZnO powders was measured using a Micromeritics Gemini V series surface area analyser.

3.3 Milling effect

Figure 3.1 shows XRD patterns of ZnO powders. The pattern of unmilled powder shows a series of strong and narrow peaks characteristic for high quality ZnO wurtzite crystals (Figure 3.1a). In contrast, the ZnO peaks in the patterns of milled materials have lower intensity and broadened as shown in Figure 3.1b,c. This effect is typical for materials after milling and attributed normally to a smaller grain size and high density of various defects. It is obvious, however, that the pattern in Figure 3.1c corresponds to a more disordered material. The peaks are noticeably smaller and broadened much stronger, suggesting structural differences between these two samples. XEDS analyses of ZnO precursors and milled ZnO powders reveal that impurities were introduced into the ZnO powders during the milling process. For example, the impurities in the sample milled under high-energy conditions

![XRD patterns of ZnO powders](image-url)
contain about 6.7 wt.% Fe, 1.3 wt.% Cr, and a negligible amount of Ni. These elements appeared in the milled sample as contaminations from the milling container and media.

To compare the evaporation patterns of different vapor sources, a series of experiments was conducted and the weight losses of ZnO powders (milled and unmilled) at 1300 °C in Ar flow after different periods of time were measured. Figure 3.2 shows the weight losses of the unmilled powder and the sample milled under high-energy conditions. It can be seen that the evaporation rate of the unmilled vapor source remains constant as its graph of weight loss is close to a straight line with time. However, this is not the case for the milled vapor source. The evaporation rate for the vapor source milled under high-energy conditions is fast in the beginning of the evaporation (the first hour) and becomes slow after 1 h of heat treatment under Ar flow at 1300 °C. Specifically, during the first 1 h heat treatment, the milled sample loses 17 wt.%, whereas the unmilled sample loses only 5%. The fact that the two plots have a similar slope after the first hour of heat treatment indicates that the samples have a similar evaporation rate. This suggests that the evaporation rate of the milled vapor source is much faster in the beginning (the first hour) and becomes similar to that of the unmilled powder afterwards. After 2.5 h of annealing, the rate of evaporation from the milled material becomes even slightly lower.

The effect of low-energy ball milling on the evaporation rate of ZnO is much less pronounced. The weight loss of this sample is only slightly higher than that of the unmilled ZnO powder. The corresponding weight loss of the sample milled under low-energy conditions after 1 h of annealing is about 6 - 7 wt.%. It may be concluded
that the degree of the enhancement of the evaporation rate depends on the mode of milling strongly. For high-energy ball milling, the amount of vapor generated in the beginning of annealing is significantly higher than that of the unmilled commercial powder. For the powder milled under low-energy conditions, the weight loss of the vapor source is only slightly higher than that of the unmilled ZnO powder.

It is well accepted that various modes of milling may lead to different products [132]. High-energy ball milling involves strong ball impacts when colliding balls possess a high value of kinetic energy. Many interesting milling effects are related to high-energy conditions [132]. Interesting phases such as supersaturated solid solutions, amorphous alloys, disordered intermetallics and quasicrystals were produced under high-energy milling conditions. Low-energy ball milling is a less violent processing mode involving mostly shearing/friction treatment and/or weak impacts. However, it could be efficient enough to trigger a number of mechanochemical reactions and to create certain disordered phases [132, 144]. Even though some phases produced by high-energy ball milling are not accessible under low-energy conditions, this mode of milling created similar phases for some materials (e.g., [119, 144–146]). In our study, we observed that high-energy ball milling produced a material with dramatically enhanced evaporation behavior while effect of low-energy ball milling was much less pronounced. We can therefore conclude that the presence of a high-energy ball impact is crucial for the dramatic enhancement of evaporation.

As ball milling is well known as a traditional technique for reducing particle size, the increase in the surface area could be suggested as a possible explanation of the evaporation behavior of ZnO powders milled under high-energy conditions. However, the surface area can even decrease slightly during milling in some cases. This is because, under the action of the colliding balls during milling, two processes are competing: particle fracturing and cold welding. Depending on the mechanical properties of a particular material, the former or latter can dominate leading to particle size refinement or increase, respectively [147]. In addition, the idea of a higher surface area does not explain dramatic changes in the evaporation rate of the milled vapour source with time. Apart from influencing the size of the particles, ball milling could induce various defects and reduce the grain size of the powder. Therefore, an alternative explanation of the evaporation behavior of milled powders could be the partial disordering of the material caused by the milling treatment.

To clarify the reason for the enhanced evaporation of the milled powders, we conducted BET surface area measurements for the unmilled ZnO powder and ZnO powders milled for 50 and 100 h under high-energy conditions. Table 3.1 shows that the surface area is about 3 - 4 m² g⁻¹ for all samples and depends weakly on the milling time. The surface area even decreases slightly after 100 h of milling. Such
Table 3.1: Surface area of ZnO powders milled under high-energy conditions for various times.

<table>
<thead>
<tr>
<th>Milling time (h)</th>
<th>Surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>50</td>
<td>3.9</td>
</tr>
<tr>
<td>100</td>
<td>3.3</td>
</tr>
</tbody>
</table>

A behavior can be explained by the particle size and mechanical properties of ZnO powder. Unlike Zn and other metals, ZnO is not a ductile material, so the refinement of particle sizes during milling is possible. However, there exists a critical particle size (called the limit of comminution) corresponding to the smallest possible size of particle that can be achieved by grinding [132]. If the particles are too small, they behave like a ductile material and tend to agglomerate. According to SEM analysis, the particle size in the ZnO precursor is smaller than 1 µm. We anticipate that this size is close to the equilibrium particle size for ZnO. During milling, the processes of cold welding and fracturing were nearly balanced, resulting in no significant change in the surface area. Since the surface areas of two materials are similar, unusual evaporation behavior of milled materials can be explained by partial disordering caused by milling.

Figure 3.3 shows TEM images of ZnO material milled under high-energy conditions. The particles have an irregular shape and a broad size distribution (not shown). Figure 3.3a shows a bright-field image of a typical particle. Its diffraction pattern (see inset) consists of a series of rings that can be associated with an amorphous or polycrystalline structure. This system of rings can be indexed by ZnO reflections, suggesting a polycrystalline structure of the material. The high-resolution image in Figure 3.3b shows the detailed structure of the particle revealing small grains with the size of 5 - 10 nm (some of them are marked with arrows).

Therefore, we can confirm the relation between the anomalous evaporation behavior and disordered structure of milled material. The particles of the milled material are agglomerates of small grains with the size of several nanometers. Such a material has a large fraction of atoms located in grain boundaries [148]. In addition, the individual grains are most probably imperfect and may contain a lot of defects such as vacancies, stacking faults and dislocations. The bonding of atoms relates to the local coordination and is supposed to be different in disordered or strained areas. We speculate that the atoms in grain boundaries and defect surface sites and strained areas are bonded more weakly than those in a high quality ZnO crystal structure. Under high temperature, such atoms tend to evaporate faster and the
vapor generation is accelerated significantly. After a certain period of time of the heat treatment, weakly bonded atoms in grain boundaries and surface defect sites evaporate or reorganize into a well-crystallized structure. Crystals with an improved structure due to defects annihilation are left. At that stage, the evaporation rate is governed by the surface area of the ZnO powders, which is similar in milled and unmilled powders. Such a simple model can explain the evolution of evaporation ability of milled ZnO powders, which is very high in the beginning and comparable with that of ZnO precursors after the first stage of annealing.

### 3.4 Growth of ZnO nanowires

As can be noted above, 1 h is the time of anomalously enhanced evaporation from the milled ZnO powders. As a consequence, 1 h is chosen to be the standard synthesis time for growing ZnO nanowires by evaporating milled ZnO powders. According to SEM and TEM investigations, a layer of nanowires was formed on the Si substrates located at a temperature zone of approximately 250 - 400 °C (at the distance of 17 - 20 cm from the vapour source).

Figure 3.4 shows a typical SEM image of a nanowire layer. The nanowires cover a large area of the substrate with a high density. The diameter of the nanowires is typically between 20 and 80 nm with the length up to tens of micrometres. The general morphology of the nanowires is the same, but the diameter of the nanowires is a function of the distance from the vapour source. Thinner nanowires form in more distant areas where the temperature is lower. No catalytic particles, typically
Figure 3.4: SEM images of ZnO nanowires. (a) Low magnification image of a nanowire layer. (b) A typical nanowire. (c) Branches of nanowires.

required for the vapor-liquid-solid growth mechanism [45], were observed at the nanowire tips. The SEM image in figure 3.4b shows the typical morphology of a nanowire. Branches developed from parent nanowires can often be observed. Figure 3.4c shows such an example. The crystal structure and composition of the ZnO nanowires obtained was confirmed by XRD and XEDS analyses. XEDS analysis did not reveal the presence of Fe, Cr or Ni in the sample, suggesting that these elements present as contaminants in the vapor source do not participate in vapor transport to the location of ZnO nanowires.
Figure 3.5: TEM images of ZnO nanowires. (a) Low resolution bright-field image. (b), (c) Nanowires with a smooth and rough surface, respectively. (d) Low resolution image of a connection area between two nanowires. (e) High resolution image of the area marked with a square in (d). (f) Selected area diffraction pattern of the connection area of the nanowires shown in (d) and (e).

Figure 3.5 shows TEM images of ZnO nanowires. The general morphology of nanowires is shown in Figure 3.5a. Generally, these nanowires can be attributed to two basic types, namely nanowires with a smooth surface (Figure 3.5b) and nanowires with a rough surface (Figure 3.5c). The number of nanowires with a rough surface is significantly larger. The surface of such nanowires is built mainly with some preferential facets. In most cases reported in the literature, ZnO nanowires grow with smooth side surfaces along the [0001], ⟨1010⟩ or ⟨11̅20⟩ directions [26] and the type of faceting reported here is a rather unusual phenomenon for ZnO. The detailed analysis of the morphology of corrugated nanowires is presented in the next chapter.

As was mentioned above, the branching of wires can often be observed in the sample. Long nanowires can join together or some shorter ZnO rods can be found on the surface of the parent nanowire. Our TEM analysis showed that all of the connec-
Figure 3.6: CL spectra of ZnO nanowires and ZnO powder taken at the accelerating voltage of 15 kV and emission current of 30 µA.

ations between branches and nanowires form a single-crystalline body. Figure 3.5d presents one of the connections between the nanowires. The high-resolution TEM image of the enlarged fragment of this connection area is shown in Figure 3.5e. According to the diffraction pattern (Figure 3.5f), a nanowire with a rough surface grows along the [0001] direction, whereas a nanowire with a smooth surface grows along the [0110] direction. It can often be observed that a nanowire with a rough surface has smooth branches or vice versa. However, this general rule has exceptions.

Figure 3.6 shows cathodoluminescence spectra of ZnO nanowires and a stoichiometric ZnO powder (Alfa Aesar). The CL spectrum of the ZnO powder shows a near-band-edge (NBE) peak centered at 390 nm (3.19 eV), which is attributed to bound and free exciton emissions [149]. The NBE emission is hardly observable in the CL spectrum of the ZnO nanowires. Piqueras et al suggested that this CL quenching is due to defects in the zinc sublattice, possibly vacancies acting as electron traps [150]. Such a strong suppression of the NBE peak is not usually observed in ZnO nanowires grown by other methods [151].

A wide green emission band centered at 510 nm (2.43 eV) dominates the CL spectrum of the nanowires. This emission band is quite typical for ZnO materials but its origin is still controversial. It is conventionally attributed to singly ionized oxygen vacancies [152] but different origins such as zinc vacancies [153], interstitial zinc ions [154], copper impurities [155] and others have also been proposed.
Dijken et al. [156, 157] explained this emission by a transition of an electron from a level close to the conduction band edge to a deeply trapped hole \( \text{Vo}^{**} \) in the bulk of the ZnO particle. The \( \text{Vo}^{**} \) centres were generated by surface trapping of photogenerated holes, followed by their transfer from the valence band to \( \text{Vo}^* \) levels in the bulk. It is also possible that the green emission was enhanced by impurities such as Fe, Cr and Ni. Indeed, these impurities were present in the milled material used as a vapor source. However, any evidence of the presence of these elements in the nanowires was not found by XEDS and TEM analysis and it is believed that they do not participate in the vapor transport and stay in the vapor source material because of the high melting points. Therefore, Fe, Cr and Ni impurities do not contribute to the detectable luminescent properties of ZnO nanowires. Regardless of the origin of the emission band, it can be a merit that the ZnO nanowires grown via the ball-milling and annealing method exhibit a dominant green emission. Such enhancement of a particular emission band is important for the applications of ZnO nanowires as a luminescent material.

3.5 Conclusions

Equal amount of the mechanically milled powder can generate more vapors upon heating than the unmilled ZnO powder in the initial stage of annealing. The effect is very strong for the sample milled under high-energy conditions (strong ball impacts) while for low-energy conditions it is not so obvious. The observed anomalous behavior of the milled material is not related to a larger surface area but is defined by a partially disordered structure induced by ball milling. The high-energy ball milling procedure causes dramatic structural changes in the powder. The enhanced evaporation is most probably caused by the presence of weakly bonded atoms in grain boundaries and surface defect sites and strained areas.

ZnO nanowires were synthesized by evaporation of the milled powder. Nanowires with rough and smooth surfaces coexist in the sample and the former morphology is dominant. The cathodoluminescence spectrum of the nanowires shows a dominant green emission band.

The results presented in this chapter have been published in

Chapter 4

Unusual corrugated nanowires of zinc oxide

4.1 Introduction

It is known that the c-axis (the [0001] direction) is the most common growth direction for ZnO nanowires [26,158]. Their typical morphological characteristics can be represented as a hexagonal prism, i.e. a hexagonal cross section and flat side walls [26]. The faceted side walls are commonly lying on \{10\overline{1}0\} or \{1\overline{1}20\} atomic planes as they have the lowest surface energies.

In this chapter, the unusual shape of nanowires grown by evaporation of a ball milled powder is analyzed. The analysis shows the zigzag side walls parallel predominantly to \{10\overline{1}1\} and \{10\overline{1}1\} facets. From the fundamental point of view, such a phenomenon is an example of stabilization of facets that do not correspond to the lowest surface energy in ZnO nanowires. From the practical viewpoint, such nanowires have an increased surface area compared to the nanowires with smooth side walls. In addition, the dominating \{10\overline{1}1\} and \{10\overline{1}1\} surface facets are polar facets in ZnO [158], which may generate new properties of ZnO for some particular applications. Yang et al. predicted that nanoscale wires dominated by \{10\overline{1}1\} and \{10\overline{1}1\} surfaces could have potential applications in sensors, transducers and biosensing [159]. Zhou et al. [160] proposed that zigzag structures are expected to have novel properties due to electron and photon scattering in zigzag structures.
4.2 Experimental

The corrugated nanowires were prepared by thermal evaporation of a ball milled ZnO powder (see the previous chapter for details). Ball milling of zinc oxide leads to a significant increase in the evaporation rate of the material. 300 mg of the milled powder were placed at the centre of a horizontal tube furnace with the temperature set at around 1300 °C. Ar gas with a flow of 0.4 l min$^{-1}$ was used as a carrier gas to transfer ZnO vapors from the central hot zone of the furnace to a cooler zone of about 250 - 400 °C where corrugated nanowires formed on Si (100) substrates.

The synthesized products were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Hitachi S-4500 scanning electron microscope and Phillips CM300 and FEI F30 transmission electron microscopes were used.

![Figure 4.1: SEM and EELS of corrugated ZnO nanowires.](image)

(a) Low-magnified SEM image. (b) and (c) high-magnified SEM images showing an individual nanowire and wire tips, respectively. (d) EELS profile of a typical nanowire.
4.3 The morphology of nanowires

Figure 4.1 is a typical SEM image of corrugated nanowires, from which a large number of nanowires with unsmoothed side walls can be clearly seen. Figure 4.1b is a high magnification image and shows a typical nanowire with zigzag side walls. Figure 4.1c shows the structural characteristics of the nanowire tips. From those aligned with the viewing directions, hexagonal shaped tips can be identified and a drawn hexagon emphasizes such a tip (Figure 4.1c). The composition of the synthesized products was determined by electron energy loss spectroscopy (EELS) attached to the TEM and Figure 4.1d shows a typical EELS profile, from which the O K and Zn L edges confirmed that the synthesized products were ZnO.

Figures 4.2a-c are bright-field TEM images and corresponding selected area electron diffraction (SAED) patterns taken from a typical nanowire viewed along different crystallographic directions. In order to produce these TEM images and SAED patterns, the nanowire was rotated along its axial direction (i.e. [0001] direction) and the three zone axes were [1100], [4510] and [1210], respectively. The surface of the nanowire consists of a sequence of surface features. The appearance of the sur-
face features is rather irregular. We found that the values of many angles between the edges of adjacent surface features in three images did not change much when the nanowire was rotated. The variation of those angles was only a few degrees. This suggests that the observed surface arrangement in the presented images is constructed by the projections of the edges of the same facets. This agrees well with the concept of a hexagonal cross section observed in SEM images if we adjust the structure of a hexagonal prism by changing each side surface of it into an alternating sequence of ascending and descending facets.

Figure 4.3a presents a distribution of the angles between the edges of adjacent surface features derived from images of nanowires viewed along the [1210] direction. The distribution has a maximum between 115-125°, which matches well with the most commonly observed surface feature, as shown in Figure 4.3b. Figure 4.3c is the corresponding atomistic model and shows a zigzag form of (10\(\bar{1}1\)) and (10\(\bar{1}\bar{1}\)) facets, from which the angle between ideal (10\(\bar{1}1\)) and (10\(\bar{1}\bar{1}\)) facets is 124°. We believe that the facets of \{10\(\bar{1}1\)\} and \{10\(\bar{1}\bar{1}\)\} families are the most common type of facets on the side walls of our nanowires, and their morphology can be approximated.
Chapter 4. Unusual corrugated nanowires of zinc oxide

Figure 4.4: 3D structural models for corrugated ZnO nanowires. (a) A basis structure of a diameter-modulated nanowire. (b) A modified model with side facets independent from each other and irregular surface features. The zigzag facets of \{10\overline{1}1\} and \{10\overline{1}\overline{1}\} families are shown in blue and red, respectively; the (0001) plane is shown in yellow.

by a hexagonal prism shape with side \{10\overline{1}0\} facets cut into the sequence of zigzag facets of \{10\overline{1}1\} and \{10\overline{1}\overline{1}\} families. The relatively broad distribution of angles in Figure 3a may be explained by the presence of surface steps on \{10\overline{1}1\} and \{10\overline{1}\overline{1}\} surfaces.

Simplified three-dimensional models of possible morphologies of ZnO nanowires with corrugated surfaces are illustrated in Figure 4.4. Although these models are only an approximation, they contain typical structural/morphological characteristics of the corrugated nanowires such as a hexagonal cross section, faceted \{10\overline{1}1\} and \{10\overline{1}\overline{1}\} side walls, reshaping of side walls of a hexagonal prism into a sequence of zigzag facets. All the shown side facets are the facets of the same \{10\overline{1}1\} and \{10\overline{1}\overline{1}\} families and their position and orientation are carefully calculated assuming that each facet has a standard 'length'. Figure 4.4a shows a basis structure of our nanowires. All the facets around the nanowire body ascend or descend simultaneously creating a diameter-modulated morphology. \{10\overline{1}1\} and \{10\overline{1}\overline{1}\} facets are shown with blue and red colors respectively. Figure 4.4b shows a more realistic modified model where facets on different sides of a hexagonal prism may be oriented independently from each other. Such a structure is simulated by random introduction of pairs of parallel facets on the opposite sides of the structure. This leads to the appearance of some 'longer' facets on the sides of a nanowire and irregular surface features.
Although the morphology of ZnO nanowires with corrugated surfaces dominated by \{10\bar{1}1\} and \{10\bar{1}1\} facets has not been reported previously, a similar morphology has been reported for GaN nanowires, another wurtzite material [160]. In fact, two basic GaN morphologies were indentified. The first type of nanowires represents nanowires with periodic zigzag shapes, and the second type corresponds to diameter-modulated nanowires. Elementary ‘unit cells’ have been suggested for explaining the assembly of these unusual nanowires. The ‘unit cell’ of diameter-modulated nanowires is described as a truncated hexpyramid formed with 12 \{10\bar{1}1\} planes and cut with two \{0002\} planes. Such a shape is identical to the shape of the basic morphology shown in Figure 4.4a. However, as we mentioned eariler, the corrugated nanowires described in this study are more complicated and cannot be described satisfactorily enough by this model only. Nevertheless, they are obviously related closely to their GaN counterparts, suggesting that similar morphologies can be produced for various materials with wurtzite structure.

The formation of crystals with particular surface facets can happen due to minimization of surface energy. However, as we mentioned before, \{10\bar{1}0\} and \{11\bar{2}0\} surfaces are the surfaces of the lowest energies in ZnO [161]. If the crystal shape corresponds to the minimum of surface energy, these facets should be exposed by the crystal. In our case, in contrast, the crystal is framed with \{10\bar{1}1\}, \{10\bar{1}1\} and some other facets, indicating that the nanowire morphology deviates from the equilibrium shape. Therefore, the corrugated morphology of nanowires must be stabilized kinetically.

A careful investigation of high resolution TEM images reveals that the nanowires possess many stacking faults lying on the (0001) atomic planes (shown in Figure 4.5a with arrows). Stacking faults are very common defects in ZnO and it is not surprising to observe them in our nanowires. However, their existence may play an important role in promoting lateral growth and stabilization of a special nanowire morphology under specific conditions. In general, stacking faults terminating at a surface can naturally introduce surface steps (Figure 4.5b). According to the theory of crystal growth and numerous experimental observations [162, 163], surface steps often act as sites of preferential adsorption of adatoms during the formation of a crystal. We believe that stacking faults in our nanowires play a role in initiating the lateral growth.

There must be, however, appropriate conditions for stacking faults to influence the morphology of a crystal. Stacking faults can be often found in nanowires but their presence does not usually lead to special morphologies. The key factor for the formation of corrugated nanowires may be the high degree of vapor supersaturation in the growth enviroment. The flow rate of the carrier gas in our case is at least
Chapter 4. Unusual corrugated nanowires of zinc oxide

Figure 4.5: Stacking faults in ZnO nanowires. (a) High-resolution TEM image of a nanowire showing stacking faults along the [0001] direction (their position is marked with arrows). (b) A model of a surface step associated with a stacking fault in wurtzite.

5 - 10 times higher than that normally used in previous reports. In addition, the ball milling of the powder used for evaporation leads to a great increase in its evaporation rate (see the previous chapter). High vapor supersaturation causes, as a consequence, a high deposition rate of adatoms onto the surface of nanowires and promotes the lateral growth.

The detailed mechanism of the lateral growth induced by stacking faults is not clear and requires further investigations. Nevertheless, it is anticipated that an initial buildup of adsorbed species around the stacking fault may lead to the surface roughness. Such a phenomenon has been observed, for example, in the formation of nanowires and quantum dots along the steps and trenches on the surfaces [164,165]. Another possible mechanism is the influence of the so called Ehrlich-Schwoebel barrier (which is described as an additional potential barrier associated with the presence of a step on the surface of the crystal [166,167]) that also may lead to the formation of surface hills in some materials [168,169].
After the formation of the initial surface roughness, a specific crystallographic direction becomes the fastest growth direction. It is expected that the lateral growth happens preferentially along the $\langle 10\overline{1}1 \rangle$ and $\langle 10\overline{1}\overline{1} \rangle$ directions. Such a growth naturally leads to the presence of $\{10\overline{1}1\}$ and $\{10\overline{1}\overline{1}\}$ facets on the surface of nanowires and the formation of triangular hills. The correlated behavior of the surface features on the six side walls of the nanowire can be explained by the influence of stacking faults that lead to the formation of quasi-symmetrical arrangement of surface hills.

The overall picture of nanowire formation can be described as follows. In the initial stage of growth, long ZnO nanowires with morphologies of hexagonal prisms are formed by a fast growth along the [0001] direction. Stacking faults in the nanowires naturally introduce steps on the side walls. Under the high vapor supersaturation environment, those stacking faults act as sites of the preferential attachment of arriving atoms, leading to the lateral growth. After the initial transient period, the $\langle 10\overline{1}1 \rangle$ and $\langle 10\overline{1}\overline{1} \rangle$ directions are becoming the fastest growth planes for the lateral growth.

4.4 Conclusions

Unusual ZnO nanowires with a hexagonal cross section and corrugated side surfaces have been produced by evaporation of a ball milled powder. Such a morphology deviates strongly from the typical growth habit of ZnO which involves flat $\{10\overline{1}0\}$ or $\{11\overline{2}0\}$ surfaces of the lowest surface energy. We found that $\{10\overline{1}1\}$ and $\{10\overline{1}\overline{1}\}$ surfaces are the most common type of surfaces in these nanowires. The morphology of nanowires can be approximated by a number of modifications of hexagonal prism morphology with flat $\{10\overline{1}0\}$ side surfaces converted into zigzag facets. The unusual morphology is attributed to the lateral growth activated by the high vapor supersaturation and the presence of stacking faults in the nanowires.

The results presented in this chapter have been published in

Chapter 5

A novel approach for mass synthesis of V$_2$O$_5$ nanorods

5.1 Introduction

Vanadium pentoxide (V$_2$O$_5$) is an example of a compound whose nanostructures possess better electrochemical properties than those of bulk crystals. This material is a traditional candidate for intercalation electrodes in Li-ion batteries and electrochromic devices [170]. However, the performance of V$_2$O$_5$ electrodes used to be significantly limited by a slow diffusion rate of lithium in the lattice and low electronic conductivity. 1D nanostructures of vanadium pentoxide are able to solve these conventional problems and provide good electrode performance [170].

Chemical methods are currently used to prepare elongated V$_2$O$_5$ nanomaterials. These approaches include hydrothermal growth [98], sol-gel synthesis [171], electrochemical deposition [97] combined, in some cases, with the use of membrane-based templates [96, 97]. Such preparation methods may involve special chemicals and equipment or particular types of templates such as polycarbonate or anodic alumina membranes with cylindrical pores. Apart from the chemical methods, thermal evaporation approach has been employed to produce nanowires and nanobelts of vanadium pentoxide recently [99, 172]. A typical product of this method is a thin layer of nanomaterials on a substrate. The analysis of the above methods suggests that a simple convenient synthetic method capable of producing elongated V$_2$O$_5$ nanomaterials in real mass quantities has not been established yet.

A novel solid-state process capable of producing large quantities of V$_2$O$_5$ belt-like nanorods is presented in this chapter. In this approach, V$_2$O$_5$ powder is mechanically milled in a ball mill first to prepare a nanocrystalline precursor and then annealed in air to produce nanorods. Nanorods form via a controlled recrystallization process during the annealing treatment. The growth process, morphology and structure
of the nanorods are presented. Electrochemical testing in LiPF$_6$ electrolyte has demonstrated an enhanced cycling stability for lithium intercalation.

5.2 Experimental

**Ball milling:** $V_2O_5$ powder (Sigma Aldrich, 99.6 % purity) was milled in argon atmosphere (excessive gas pressure of 100 kPa) in a steel magneto-ball mill for 100 h at room temperature. Three grams of $V_2O_5$ powder were loaded inside the milling container and four hardened steel balls (diameter of 25.4 mm) were used as milling media. The magnet was located at the bottom of the mill at a 45° position in relation to the vertical direction to create strong milling impacts at the rotating speed of 160 rpm. The as-milled powder was annealed in two different ways: (1) as a static thin layer on top of a substrate inside a tube furnace; (2) in a fluidized bed.

**Static isothermal annealing:** A thin layer of milled material was deposited onto the surface of a steel or oxidized silicon substrate. The layer density was typically about 3 mg cm$^{-2}$. The substrates covered with the milled $V_2O_5$ powder were isothermally heated at 630 °C for different times (between 1 minute and several hours). A conventional high temperature furnace (Carbolite CFM 14/2, Sheffield, England) with a horizontal quartz tube was used for the annealing, which can be performed in air (open ends of the quartz tube) or in high purity O$_2$ flow. The substrates coated with $V_2O_5$ were inserted into the preheated furnace and pulled out quickly after the desired time of annealing.

**Annealing in a fluidized bed:** The fluidized bed conditions were achieved by vibrating a cylindrical quartz reactor with a diameter of 40 mm and a height of 200 mm. 1 g of the milled $V_2O_5$ powder was placed into the reactor, and the reactor was inserted into the furnace preheated to 600 °C. After the insertion into the furnace, the reactor was vibrated vertically with a frequency of 20 Hz and the amplitude of vibration of 1 mm. A flow of air passed through the reactor at the same time. The reactor was kept in the furnace for 60 minutes after the temperature in it reached 600 °C (heating up the reactor and its content requires about 12 minutes after it is placed into the furnace).

**Electrochemical testing:** The nanorods, obtained in a static layer at 630 °C in air after 5 min of annealing, were used to assemble the working electrode by scratching them away from the substrate surface and mixing with carbon black and a binder. Active material - $V_2O_5$ (80 %), carbon black (10 %) and polyvinylidene fluoride (PVDF) (10 %) binder in N-Methylpyrrolidone (NMP) were homogeneously mixed using a mortar. Resulting slurry was pasted onto aluminum foil and dried in vacuum at 120 °C for 12 h to remove the NMP solvent. The electrode was then
pressed in the form of a disc with diameter of 14 mm and dried in vacuum again at 120 °C for 1 h to minimize the moisture content. A coin cell was fabricated to test the charge/discharge performance. The cell was assembled in a glove box (H₂O, O₂ ≤ 0.1 ppm, Mbraun, Unilab, USA). The electrolyte was 1 M LiPF₆ in a mixture of EC and DMC (1 : 1 by volume, provided by MERCK KgaA, Germany) and with microporous polypropylene film as a separator. The cell was charged and discharged at the current rate of 10 mA g⁻¹ over the voltage range of 1.5 - 3.5 V vs. Li/Li⁺. The electrochemical test was carried out at room temperature (25 °C).

5.3 Growth of V₂O₅ nanorods

The shape transformations of the ball milled powder as a function of the annealing time are shown in Figure 5.1. The SEM image in Figure 5.1a shows the typical agglomerates of the mechanically milled V₂O₅ powder that consist of particles of various sizes with irregular shapes. After the sample is heated at 630 °C in air on a substrate, SEM analysis reveals a spectacular reorganization of the particles into a layer of elongated sheets. The morphology of the material shows almost complete shape transformation from particles to belt-like nanorods. The morphology changes of V₂O₅ powders after 5, 10 and 30 minutes of annealing are shown in Figures 5.1b, 5.1c and 5.1d, respectively. The nanorods have a rectangular cross section and nearly round tips. Their surface is clearly dominated by a particular type of facets that occupies 50 - 80 % of all the surface of nanorods. The typical width of the nanorods grown after 5 min is in the range of 150 - 300 nm, the thickness is between 60 and 100 nm, and the length is up to several micrometers. The same elongated shape with a rectangular cross section is preserved after prolonged heating, and the longer time of annealing results in an increased aspect ratio and general enlargement of nanorods. The SEM examination shows that the quantity of nanorods per unit of area gets smaller, suggesting that some small nanorods have been consumed to promote the further growth of larger ones.

Figure 5.2 shows an XRD pattern of nanorods. The observed peaks correlate with strong lines of crystalline vanadium pentoxide phase (PDF file 41 - 1426), confirming the phase composition of nanorods. A broad feature at about 39 - 40 degrees is due to a minor amount of iron and chromium oxides (the oxides have strongest lines around this position and the overlap of the corresponding X-ray reflections produces the observed broad hill). Contamination of a milled powder by the material of the milling vial and balls is typical for ball milling and iron and chromium originate from the steel material of the milling device used.
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Figure 5.1: The transformation of ball milled $\text{V}_2\text{O}_5$ powders into nanorods. SEM images of as-milled powders (a) and the material after subsequent annealing in air at 630 °C for 5, 10 and 30 minutes (b, c, and d, respectively).

Figure 5.2: XRD pattern of nanorods
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TEM was employed to reveal the structure of \( V_2O_5 \) nanorods. Figure 5.3a shows a bright-field image of a typical nanorod, and the inserted selected area electron diffraction pattern indicates a single-crystalline structure elongated along the \([010]\) direction. Figure 5.3b shows a high resolution TEM image of a part of the nanorod, revealing a two dimensional lattice. Based on the results from TEM and SEM analyses, a model demonstrating the typical shape of \( V_2O_5 \) nanorods was created (Figure 5.3c). The nanorod has a rectangular cross section and its surface is occupied mostly by \{001\} facets. Another pair of side surfaces is \{100\} surfaces and their relative width is smaller. The circular-like tip of a typical nanorod is formed by a combination of \{310\}, \{010\} and \{-310\} facets. Please note that we use a definition of the orthorhombic unit cell with principal axes \( a = 11.51 \text{ Å}, b = 3.56 \text{ Å}, c = 4.37 \text{ Å} \) to index the planes and directions (another definition of the unit cell with interchanged \( b \) and \( c \) axes is also commonly used in the literature).

To reveal the mechanism of growth, the milled precursor and the structure of the material at the early stages of growth were studied in detail. Figure 5.4 shows the results of the analysis of the milled powder. The XRD pattern (Figure 5.4a) reveals a series of peaks that can be indexed as \( V_2O_5 \) reflections (PDF file 41 - 1426). The
peaks have low intensity and significantly broadened. Most of them are shifted from their positions typical for perfect stoichiometric \( \text{V}_2\text{O}_5 \) (shown as red lines in the XRD pattern). The shift is towards the lower values of \( 2\theta \) (i.e. towards larger spacings between the lattice planes) for most of the peaks but the contraction of the some lattice distances is also observed. For example, (411) reflection is slightly shifted towards higher double angles (not shown), indicating a decrease in the spacing between the corresponding planes. The XRD data are generally consistent with the predicted grain refinement and increase of strain in ball milled \( \text{V}_2\text{O}_5 \). In addition, the distortion of \( \text{V}_2\text{O}_5 \) lattice leading to the changes of lattice plane distances is detected.

TEM image in Figure 5.4b shows the general morphology of the milled powder. The particles have irregular shapes and sizes in a wide range between 30 nm and 1 \( \mu \)m. Particles larger than 1 \( \mu \)m are also observed. A bright-field image of a typical particle and the corresponding SAED pattern are given in Figures 5.4c and 5.4d, respectively. The contrast variations in the particle’s image indicate that it consists of nanoscale grains and the diffraction pattern in the form of rings is consistent with this observation. Grains with typical sizes in the range of 7 - 35 nm are observed in the sample (Figure 5.4e). Their relative orientation is random. The measured BET surface area of the milled powder is 10 m\(^2\) g\(^{-1}\). Strictly speaking, the particles in the milled powder should be understood not as individual polycrystalline particles but as porous aggregates of polycrystalline nanoparticles attached to each other. Such aggregates are typical for ball milled materials and are formed as the result of repeated fracturing and cold welding in the course of ball milling.

The ring pattern in the Figure 5.4d is generally consistent with \( \text{V}_2\text{O}_5 \) reflections. The more careful investigation reveals, however, that the rings are shifted from their anticipated positions for \( \text{V}_2\text{O}_5 \). The dots in the same ring have slightly varied distances between them and the centre of the pattern. Some rings that are close to each other enough (e.g. 001 (\( d_{001} = 4.38 \) Å) and 101 (\( d_{101} = 4.09 \) Å) rings) tend to merge and the boundary between them is not clearly distinguishable. The values of lattice distances are different from the ideal ones in \( \text{V}_2\text{O}_5 \) and significant variations in the degree of their deviation from the ideal positions exist in various grains. Table 5.1 summarizes values of some lattice distances derived from X-ray and electron diffraction data. The values of d-spacings for ideal \( \text{V}_2\text{O}_5 \) crystals are also given for comparison.

The ESR spectrum of the milled powder is shown in Figure 5.4f. A single line centered at the magnetic field of about 3400 Gauss can be observed. The pure stoichiometric \( \text{V}_2\text{O}_5 \) is EPR-silent, and the resonance signal in its ESR spectrum
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Figure 5.4: The results of the analysis of the milled $V_2O_5$ powder. (a) XRD pattern, (b,c) bright-field images of the milled material. (d, e) SAED pattern and high-resolution TEM image taken from the aggregate in (c), (f) ESR spectrum of the milled material.
Table 5.1: Lattice distances in the milled V$_2$O$_5$ calculated from x-ray and electron diffraction.

<table>
<thead>
<tr>
<th></th>
<th>d$_{200}$, Å</th>
<th>d$<em>{001}$ and d$</em>{101}$, Å</th>
<th>d$_{110}$, Å</th>
<th>d$_{411}$, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray diffraction</td>
<td>5.83</td>
<td>4.44 (001) and 4.12 (101)</td>
<td>3.41</td>
<td>1.98</td>
</tr>
<tr>
<td>Electron diffraction</td>
<td>5.85 - 6.09$^a$</td>
<td>4.11 - 4.24$^a$</td>
<td>3.32 - 3.42$^a$</td>
<td>$b$</td>
</tr>
<tr>
<td>Ideal d$_{hkl}$</td>
<td>5.77</td>
<td>4.38 (001) and 4.09 (101)</td>
<td>3.41</td>
<td>1.99</td>
</tr>
</tbody>
</table>

$^a$Broadened ring with varied positions of the spots
$^b$No data

should be attributed to the appearance of paramagnetic V$^{4+}$ species in the lattice. Particularly, isolated V$^{4+}$ species yield a signal with a well resolved hyperfine structure while clustered V$^{4+}$ species yield a single symmetrical line [173]. The ESR data suggest that the milled sample is partially reduced and explain the observed lattice distortions in the material.

The above findings are mostly consistent with the previous studies of ball milled V$_2$O$_5$ powders [174–176]. Su et al. [174] reported a significant reduction of ball milled material. Electron energy loss spectroscopy (EELS) studies revealed the dominant V$^{3+}$ and V$^{4+}$ oxidation states at the edges of milled aggregates. The aggregates were dramatically reduced at the surface while the average oxidation state in their interior was 4.8. The ESR measurements detected a signal with a hyperfine structure [175] and the positions of reflections in the XRD pattern of milled V$_2$O$_5$ materials were unchanged. It indicates the higher degree of vanadium pentoxide reduction in this study. It was also proposed [174] that certain amount of amorphous phase of vanadium oxide exists in the milled particles. In contrast to the reported data, the difference in the degree of reduction between the bulk and exterior of the milled particles was not detected and the presence of the amorphous component was not observed although its presence cannot be fully ruled out.

The SEM and TEM data for powders annealed at 600 °C for short times of 1 and 2.5 min are shown in Figure 5.5. The SEM image (Figure 5.5a) shows the surface topography of the material heated for one min. The surface has a clearly observable relief and can be interpreted as an agglomeration of numerous nanoscale particles. The nanoscale particles sit close to each other and do not modify significantly the shape of their agglomerate (a large particle in the low resolution TEM image in Figure 5.5b). The high resolution TEM image (Figure 5.5c) visualizes individual single-crystalline elongated particles composing the agglomerate. Their
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Figure 5.5: Analysis of the milled powder at early stages of growth: (a, b) SEM and bright-field TEM images of the material annealed for 1 min, (c) HRTEM image of the part of the aggregate, (d) SAED pattern of the aggregate shown in (b), (e, f) SEM and bright-field TEM images of the material annealed for 2.5 min, (g) HRTEM image of the part of the aggregate, (h) SAED pattern of the aggregate shown in (f).

typical length is about 40 - 50 nm and the observed width of their projections is about 20 nm. Pores (empty space) exist between the particles and their area of contact (i.e. particle-to-particle boundaries) is limited. The electron diffraction pattern of the agglomerate is given in Figure 5.5d. It consists of a somewhat chaotic array of dots. A number of rings still can be distinguished in the pattern but the positions of individual dots vary widely, indicating a distribution of lattice spacings in the material. A system of rings observed initially in the milled material (Figure 5.4d) gets strongly distorted. This is an indication of the oxidation process happening in air at 600 °C. The missing oxygen atoms get incorporated into the distorted lattices of initial milled particles leading to changes in the lattice spacings. The oxidation process is probably inhomogeneous and starts from the surface of the agglomerates. This leads to a range of lattice spacings observed after one minute of annealing.

The SEM and TEM images of the material annealed at 600 °C for 2.5 min (Figures 5.5e and 5.5f) reveal that the agglomerates consist of enlarged nanoscale particles at this stage. Some of the particles represent a chip-like morphology where one of the dimensions is reduced and another one is increased. The empty spaces (pores) exist between individual particles in the agglomerate. The individual particles are clearly enlarged in a non-uniform fashion (Figure 5.5g). Particular crystallographic directions tend to grow faster and this leads to a preferential elongation of particles. The relatively chaotic diffraction pattern of the material after one min of annealing...
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(Figure 5.5c) changes into a clear system of rings (Figure 5.5h). The lattice distances are still, however, different from those in stoichiometric \( V_2O_5 \). The color of the material is dark red, indicating the difference in structure and optical properties from typically yellow-orange stoichiometric vanadium pentoxide. It is necessary to note that the number of dots in each ring in the diffraction pattern of the material after 2.5 min of annealing is limited, indicating a reduced number of individual particles in the agglomerate. The enlargement of particles is accompanied, therefore, by a decrease in their number. A fraction of the particles has to be consumed to build larger ones.

The morphologies of nanorods after 5, 10 and 30 min of annealing were shown earlier in Figure 5.1b,c,d. At these stages, the material is fully oxidized to reach the stoichiometric \( V_2O_5 \) composition, which is evident from the typical yellow-orange color. The growth of nanorods speeds up noticeably after \( V_2O_5 \) reaches a proper stoichiometry. The results of TEM characterization of a typical nanorod are shown above in Figure 5.3, and the observed lattice distances are consistent with those of vanadium pentoxide. The [010] direction acts as a direction of the fast growth while the apparent growth rates along [100] and [001] are much slower. The active elongation of \( V_2O_5 \) nanorods happens up to 15 min and slow changes in the size of crystals are detectable after that. The difference between sizes of nanorods is clear in Figures 5.1b and 5.1c (5 and 10 min of annealing) while the size difference between 10 and 30 min is not so pronounced.

The observed nanorod growth can be interpreted as a recrystallization process driven by the minimization of surface energy. \( V_2O_5 \) has a layered structure with basal \{001\} planes bonded weakly to each other. The surface energy of the \{001\} atomic planes is, therefore, the smallest because only a limited number of bonds are destroyed when the material is cleaved along these planes. According to the numerical simulation \[177\], the \{001\} planes have a value of surface energy of about 0.7 J m\(^{-2}\), which is significantly smaller than the calculated values for other low-energy surfaces. The growth and equilibrium \( V_2O_5 \) morphologies have to be dominated, therefore, by \{001\} surfaces, which is in agreement with the experimental data on the crystal habit of \( V_2O_5 \) nanorods. The surface of the nanorods in this study is preferentially covered (50 - 80 %) by \{001\} facets. The growth of nanorods leads to the decrease in total surface area, while the morphology stays dominated by \{001\} surfaces.

We believe that surface migration (diffusion) plays an important role in nanorod growth. The growth temperature is approaching the melting point of \( V_2O_5 \) (690 °C \[178\]), and a high degree of the surface mobility is expected at this temperature. The evidences of surface mobility processes have been found in SEM images. The
formation of new layers on the existing \{001\} planes is observed for many nanorods, indicating the flow of newly arriving surface species towards the tips of nanorods. Figure 5.6a and 5.6b present the SEM images of nanorods and the formation of new layers (shown with arrows) can be observed on the \{001\} surfaces. The active role of the surface diffusion can be a common phenomenon in the processes of solid-state growth of elongated nanomaterials from powders. It was considered responsible for the solid state formation of carbon and boron nitride nanotubes from ball milled powders [179].

The transformation of smaller nanorods into larger ones occurs during extended annealing. Nanorods form at the early stage of annealing and grow gradually during the annealing. When nanorods came to contact, we observed a number of nanorod pairs that were apparently at the various stages of merging. An example of the detected coalescence behavior of pairs of adjacent nanorods is shown in Figure 5.6c. The merging process involves active surface migration as well as the movement and subsequent annihilation of the grain boundary between the crystals of adjacent nanorods. The coalescence of adjacent nanorods ends when a single crystal with the [010] direction of preferential elongation and a larger shape forms.

The preparation of a nanocrystalline precursor by ball milling is a crucial step for the growth of nanoscale rods. We heated an unmilled V$_2$O$_5$ powder under the same conditions and only large elongated crystals in micrometer range were obtained. Although a similar elongation phenomenon takes place for the commercial powder, nanoscale rods cannot be produced. The recrystallization involves the enlargement of particles and, therefore, the nanosized crystals in the precursor created by high-energy ball milling [148] are the key to the formation of small nanorods.
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The formation of nanorods is an atmosphere-sensitive process. When oxygen-containing atmosphere (such as air or high-purity oxygen) is used, nanorods with large aspect ratios are formed, while the annealing of the milled sample in argon atmosphere led only to slightly elongated particles with much larger size. These differences can be explained by reduction of vanadium pentoxide in the course of ball milling. In contrast to V$_2$O$_5$ (melting point 690 °C), the oxides of vanadium with oxidation states V$^{4+}$ and V$^{3+}$ (such as, for example, VO$_2$ and V$_2$O$_3$) and V$_6$O$_{13}$ (which is a compound with mixed V$^{4+}$ and V$^{5+}$ ions) are typically very stable and have high melting points equal or above 1500 °C. If the starting material for the synthesis of nanorods is significantly reduced, the surface mobility is expected to be decreased and a preliminary oxidation is necessary to induce the efficient transformation of the precursor to nanorods. This can be achieved by applying an oxygen-containing atmosphere, and the transformation is suppressed in oxygen-free environments.

The scheme of nanocrystalline V$_2$O$_5$ recrystallization at 600 °C is summarized in Figure 5.7. At the initial stage of recrystallization, the aggregates of polycrystalline nanoparticles tend to remove numerous grain boundaries and transform into aggregates of single-crystalline particles with a larger size and a limited area of contact between them. The oxidation of the initially reduced materials into stoichiometric V$_2$O$_5$ happens between 1 and 5 minutes of annealing, activating the fast surface migration. The morphology of single-crystalline nanorods dominated by the low energy {001} surfaces and with the [010] growth direction appears next. The nanorods enlarge via their coalescence.
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Figure 5.8: 1 g of V$_2$O$_5$ nanorod powder obtained after annealing for 1 h in a fluidized bed at 600 °C. (a) A photograph of as-produced powder (a paper ruler is placed next to the sample), (b) SEM image, revealing the morphology of individual nanorods.

The nanorod growth in this study requires space for shape transformation from particles to elongated nanorods; otherwise nanorods will join together to form large crystals (sintering). When bulk amounts of the milled powder are heated, the material tends to aggregate into large bricks due to sintering. Therefore, a thin layer of the milled material (3 mg cm$^{-2}$) must be prepared in the case of annealing in a static layer on top of a substrate and large quantities of nanorods cannot be produced in such a procedure. A different annealing approach capable of minimizing the sintering of milled powder and producing V$_2$O$_5$ nanorod powder in large quantities is needed. Annealing in a fluidized bed can solve the problem of sintering and is able to produce mass quantities of nanorods.

Indeed, Figure 5.8a shows the photograph of the powder product of annealing in a fluidized bed. A paper ruler indicates the scale of mass production. The SEM image in Figure 5.8b reveals the nanorod morphology of the final product. Unlike the samples annealed as a static layer on a substrate, the V$_2$O$_5$ sample remains in free powder form after annealing in a fluidized bed. The particles in a range of sizes between tens of micrometers and several millimeters are visible. Weak agglomerates can be broken to smaller particles and individual nanorods easily. If required, a fraction with required sizes can be separated by sieving.

The method involving ball milling and annealing in a fluidized bed is capable of producing real mass quantities of nanomaterials. Both mechanical milling and
fluidized bed technology have been demonstrated earlier to be capable of scaling up. The large commercial ball mills were developed to produce oxide strengthened alloys and the mechanical milling and alloying is an accepted industrial process [132]. Large quantities of boron nitride nanotubes have been produced by ball milling combined with subsequent annealing [117]. The fluidized bed technology has been applied to the production of carbon nanotubes and nanofibers in the form of small granules in kilogram quantities [180].

5.4 Electrochemical properties of nanorods

Figure 5.9 shows the results of the preliminary electrochemical testing in LiPF$_6$ electrolyte. The voltage-capacity discharge profiles of the first four charge/discharge cycles at the current rate of 10 mA g$^{-1}$ are shown in Figure 5.9a. The discharge curve of the first cycle has several plateaus and voltage drops corresponding to phase changes. Indeed, it is known that V$_2$O$_5$ can be sequentially transformed into several Li$_x$V$_2$O$_5$ phases depending on the amount of lithium inserted. $\alpha$- ($x < 0.01$), $\varepsilon$- ($0.35 < x < 0.7$), $\delta$- ($x = 1$), $\gamma$- ($1 < x < 3$) and $\omega$- ($x = 3$) phases can be observed when more and more lithium is intercalated into vanadium oxide [170]. A single slope discharge curve in the second and subsequent cycles (Figure 5.9a) is characteristic for cycling of $\omega$-Li$_x$V$_2$O$_5$ phase, which cycles in a single solid-solution phase [170].

Figure 5.9b shows the specific capacity of the first 50 cycles. Starting from the second cycle, the nanorods maintain a stable capacity of around 260 mAh g$^{-1}$ with no sign of significant degradation. The cycling performance of a number of V$_2$O$_5$ nanomaterials has been studied before, and noticeable degradation of the working electrode is commonly observed after the first few cycles [181–184]. For example, an outstanding initial capacity of 1240 mAh g$^{-1}$ of a platelet-structured V$_2$O$_5$ film drops to about 200 mAh g$^{-1}$ after 20 cycles [184]. In contrast, the V$_2$O$_5$ nanorods in our study demonstrate a good cycling stability, which can be correlated to their small size and beneficial crystal orientation. Indeed, lithium intercalation into V$_2$O$_5$ nanobelts and belt-like nanowires with the identical crystal orientations has been studied earlier [99,172]. Chan et al. [99] reported fast, completely reversible lithium intercalation into V$_2$O$_5$ nanobelts. Each nanobelt could charge/discharge within a short time of several seconds without damaging the structure. Cheng et al. [172] demonstrated an efficient electrochromic device with short switching time and excellent (more than 1000 cycles) cycling stability based on lithium intercalation into belt-like V$_2$O$_5$ nanowires. The stable electrochemical performance of V$_2$O$_5$ nanorods can be attributed to the beneficial crystal orientations with suppressed thickness
Figure 5.9: Electrochemical testing in LiPF$_6$ electrolyte. (a) Voltage vs capacity discharge curves of V$_2$O$_5$ electrode cycled between 1.5 and 3.5 V versus Li/Li$^+$ at a current density rate of 10 mA g$^{-1}$. (b) Charge and discharge capacities as functions of cycle number.
along the [001] direction, which can withstand significant stresses without disintegration.

Unlike previous reports [99, 172], in which belt-like nanorods were produced by thermal evaporation, we present a distinctly different approach to grow these structures. Thermal evaporation typically produces a very limited amount of material (about 1 mg or less), while our proof-of-concept test demonstrated the production of V$_2$O$_5$ nanorods at a large scale.

### 5.5 Conclusions

A potential mass-production method for nanorods has been demonstrated. V$_2$O$_5$ nanorods in free powder or thin film forms can be produced by heating ball milled powders at about 600 °C using different annealing conditions. In particular, a fluidized bed is capable of preparing mass quantities of V$_2$O$_5$ nanorod samples. The nanorods are formed through a solid-state recrystallization of nanocrystalline V$_2$O$_5$ created by high-energy ball milling. The growth of the nanorods dominated with \{001\} facets is driven by the minimization of surface energy, and surface diffusion plays an important role in the growth process. The beneficial crystal orientation of V$_2$O$_5$ nanorods with suppressed thickness along the [001] direction provides an improved cycling stability for lithium intercalation.

Main results of this chapter have been published in

Chapter 6

Synthesis of compounds of vanadium by reduction of V$_2$O$_5$

6.1 Introduction

Preparation of V$_2$O$_5$ nanomaterials has attracted a large deal of attention in the last decade and synthesis strategies for a number of morphologies have been developed. Nanotubes [185], nanowires [186], nanorods [97], nanoparticles [187] and other types of structures are reported, including ordered arrays attached to surfaces [97, 188]. Synthesis techniques for nanomaterials of other vanadium oxides and compounds are not so well developed, and it is still difficult to obtain a desired morphology of a particular compound of vanadium. One of the ways to resolve this issue is to find an efficient way of converting the available V$_2$O$_5$ materials into those of other vanadium compounds with conservation of their morphology. Nanomaterials of other phases mimicking the morphology of V$_2$O$_5$ precursors could be obtained in such a way.

The interesting feature of the family of vanadium compounds is that the melting point of V$_2$O$_5$ (690 °C), a compound where vanadium is in the oxidation state of +5, is noticeably lower than the melting points of vanadium compounds with lower vanadium oxidation states. For example, the melting points of VO$_2$, V$_2$O$_3$, VO and VN are 1967, 1970, 1790 and 2050 °C, respectively [189]. The gap between the melting points of these compounds and that of V$_2$O$_5$ is more than 1000 °C. If the oxygen loss in V$_2$O$_5$ or its reaction with a gaseous compound is induced at a moderate temperature (below the melting point of V$_2$O$_5$), it can be expected that vanadium pentoxide can be converted into oxides and compounds with higher melting points by a single or multiple solid-state phase transformations. Since the reaction temperature is much lower than the meting point of resulting compounds, the physical processes such as evaporation, surface diffusion and sintering that may lead to shape changes are suppressed.
The reduction of $V_2O_5$ by various treatments has been reported in the literature. Vacuum [190–192] or reducing gases such as $H_2$ [193–195], $NH_3$ [91, 196, 197] and $CH_4$ [197] can be used. The vacuum treatment leads usually to the oxygen loss in $V_2O_5$ and formation of oxides with lower oxidation states such as $VO_2$ [191] and $V_2O_3$ [192]. $H_2$ reduction produces $V_2O_3$ at moderate temperatures (below 800 °C) [193, 195]. Methane treatment may lead to the formation of vanadium carbide [197]. $NH_3$ reduction is a convenient way to produce vanadium nitride [91]. The morphological changes are not investigated well in most of the studies, and the focus is usually on the phase of reduced materials and their surface area measured by the low-temperature $N_2$ adsorption.

In this chapter, the reduction of $V_2O_5$ by two approaches, vacuum and $NH_3$ reduction, is studied. The formation of three phases ($VO_2$(B), $V_2O_3$ and VN) is demonstrated and morphological changes during the reduction process are evaluated. Additional attention is given to the internal structure (texture) of the produced vanadium nitride.

### 6.2 Experimental

$V_2O_5$ nanorods (described earlier in Chapter 5) were used for studying the formation of other vanadium compounds by reduction techniques. The nanorods were produced by heating ball milled $V_2O_5$ powders in air for 5 - 10 minutes at about 630 °C. In addition to nanorods, commercial $V_2O_5$ powder from Sigma Aldrich (99.6 % purity) was used to study the formation of vanadium nitride.

Vacuum reduction of $V_2O_5$ nanorods was performed in a conventional tube furnace (Lindberg/Blue M STF 54233C, USA). One end of the quartz tube placed in the furnace was attached to a rotary pump (JAVAC DD 40). The pump was capable of creating vacuum of $10^{-1}$ torr inside the tube. The quartz tube with a sample (10 mg of nanorods) located in the tube center was vacuumed at room temperature first and the temperature was gradually increased to the desired value afterwards. The sample was kept at the stationary temperature for 2 hours and then cooled down to room temperature overnight in vacuum.

Temperature-programmed reduction of $V_2O_5$ materials by ammonia was performed in a tube furnace (Jetlow furnaces, Melbourne, Australia). The $NH_3$ flow of a pre-defined flow rate in the range of 0.7 - 2.4 l min$^{-1}$ was passing through the tube. 600 mg of $V_2O_5$ precursors were loaded inside of the tube. The samples were heated up to 700 °C at the heating rate of 2.8 - 11 °C min$^{-1}$ and kept at 700 °C for 1 hour. After that, the furnace cooled down naturally overnight in $NH_3$ flow. The as-prepared samples were passivated by flowing 0.1% $O_2$ in high purity Ar gas over
the sample for 2 hours.

Initial V$_2$O$_5$ and materials after reduction in vacuum and NH$_3$ were analyzed by a number of techniques. The phase composition was identified using X-Ray diffraction (XRD, Philips analytical x-ray spectrometer with Co radiation $\lambda = 0.1789$ nm). The morphology of materials was evaluated by scanning electron microscopy (SEM, Hitachi S-4500 instrument). More detailed structural study has been conducted in a transmission electron microscope (TEM, Phillips CM300 instrument). Surface areas and pore size distributions of vanadium nitride were evaluated using low-temperature N$_2$ adsorption (Micromeritics Gemini V series surface area analyzer and Quantachrome instruments Quadrasorb SI). The specific surface areas were calculated from the N$_2$ adsorption isotherm using the Brunauer-Emmett-Teller (BET) equation and the pore size distribution was obtained from Barrett-Joiner-Halenda (BJH) method.

### 6.3 Analysis of the reduced materials

#### 6.3.1 Reduction in vacuum

Figure 6.1 shows SEM images of the products of vacuum reduction of V$_2$O$_5$ nanorods at various temperatures. It is evident from low magnification SEM images (Figure 6.1a, c and e) that the nanorods retain the overall initial morphology, i.e. the reduction process is pseudomorphic. Figure 6.1b,d,f shows individual nanorods obtained after vacuum reduction at 400, 600 and 750 °C, respectively. The overall shape of nanorods stays the same, while the roughness of their side surfaces increases with temperature. Minor deviations from the initial shape are observed at 400 °C. The roughness increases considerably at 600 °C and the most significant changes in the degree of roughness are evident at 750 °C. The increase in the surface roughness coincides with the creation of porosity (holes and cracks in the body of nanorods).

The phases of produced nanorods were investigated by XRD and the diffraction patterns are shown in Figure 6.2. According to Figure 6.2, the dominating phase in the sample produced at 400 °C can be identified as VO$_2$(B) phase (PDF files 31 - 1438 and 81 - 2392) while the nanorods obtained at 600 and 750 °C belong to the V$_2$O$_3$ phase (PDF file 85 - 1411). These results confirm that V$_2$O$_5$ nanorods progressively lose oxygen when they are heated in vacuum. VO$_2$(B) phase is a metastable phase of vanadium dioxide, which is often found to form when VO$_2$ is produced hydrothermally [198]. Nanorods obtained at 600 and 750 °C belong to the same phase of V$_2$O$_3$ but their morphologies are apparently different. Those obtained at the higher temperature have more evident porosity and rougher surfaces. Some material deposits were detected on the substrates placed next to the sample.
Chapter 6. Synthesis of compounds of vanadium by reduction of \( \text{V}_2\text{O}_5 \)

Figure 6.1: Nanorods obtained by vacuum reduction: (a, b) at 400 °C; (c, d) at 600 °C; (e, f) at 750 °C.

annealed in vacuum at 750 °C. Certain degree of evaporation is, therefore, obvious at this temperature. This effect may contribute additionally to the development of porosity and surface roughness.

The phase transformations of single-crystalline \( \text{V}_2\text{O}_5 \) in a TEM column (high vacuum of \( 10^{-7} \) torr) were studied earlier by Su and Schlögl [190]. They also found that \( \text{V}_2\text{O}_5 \) was transformed into \( \text{VO}_2 \) at 400 - 500 °C and into \( \text{V}_2\text{O}_3 \) at 600 °C. \( \text{V}_2\text{O}_5 \) was also heated in their experiments in a vacuum of \( 10^{-4} \) torr in a sealed glass tube overnight at 400 and 550 °C and such a treatment did not produce significant changes in \( \text{V}_2\text{O}_5 \). The latter observation is not in agreement with the findings of this study.
Chapter 6. Synthesis of compounds of vanadium by reduction of $V_2O_5$

Figure 6.2: XRD patterns of nanorods obtained by vacuum reduction. (a) at 400 °C, (b) at 600 °C, (c) at 750 °C. v - peaks of $VO_2(B)$ phase, x - peaks of $V_2O_3$ phase.

The possible reason for that is degradation of vacuum in the sealed tube due to some minor oxygen loss from the $V_2O_5$ sample. If the quality of vacuum is reduced by several orders of magnitude, it may prevent significant oxygen escape from vanadium pentoxide. The authors did not provide the dimensions of the sealed tube and the amount of the sample placed inside of it and it is not possible to estimate if this can be the case. In contrast to previous findings [190], it is demonstrated here that $VO_2(B)$ and $V_2O_3$ phases of vanadium oxide can be produced by heating in a poor vacuum as low as $10^{-1}$ torr if the sample chamber is pumped all the time (dynamic vacuum condition).

It is important to note that the $VO_2$ phase obtained by Su and Schlögl in a high vacuum is the stable rutile phase of $VO_2$ and is different from $VO_2(B)$ phase obtained in this study under the vacuum of $10^{-1}$ torr. My data and the findings of Ningyi et al. [191] support the idea that there is a certain critical level of vacuum that defines which phase of $VO_2$ forms by reduction of $V_2O_5$. In the latter publication, $V_2O_5$ films were annealed at a pressure below $1.5 \times 10^{-2}$ torr, which is about one order of magnitude better than the vacuum used here. The formation of $VO_2(B)$ phase was observed at 400 - 480 °C and it was partially converted further into the stable rutile phase of $VO_2$ after some time at the stationary temperature. The formation of a particular $VO_2$ phase may depend on how quickly oxygen escapes from vanadium oxide. This process is quicker in high vacuum (such as $10^{-7}$ torr [190]) and relatively slow at the pressure of $10^{-1}$ torr. The boundary between conditions favouring the formation of $VO_2(B)$ and $VO_2(R)$ is approximately at the level of $10^{-2}$ torr.
6.3.2 Reduction by NH$_3$

Figure 6.3 shows XRD patterns of the samples obtained by ammonia reduction of V$_2$O$_5$. The samples (600 mg) of V$_2$O$_5$ were heated up to 700 °C at the heating rate of 2.8 °C min$^{-1}$ in NH$_3$ flow of 0.7 l min$^{-1}$ and kept at 700 °C for 1 hour. The peaks in the patterns fit those of cubic vanadium nitride (PDF file 73 - 0528). The peaks are broadened, indicating a small size of individual crystallites. VN-1 denotes the sample obtained from commercial V$_2$O$_5$ powder and VN-2 denotes the sample obtained from V$_2$O$_5$ nanorods.

SEM images of the initial V$_2$O$_5$ materials and the resulting VN samples are shown in Figure 6.4. Two vanadium pentoxide precursors with distinctly different morphologies were chosen in this study. The first precursor (a commercially available V$_2$O$_5$ powder) contained large particles (which are, in fact, aggregates of smaller submicron particles) with sizes of 200 - 500 micron. A typical particle is shown in Figure 6.4a. A representative VN particle obtained by the reduction of commercial V$_2$O$_5$ powder is shown in Figure 6.4b. It is easy to conclude from the comparison of Figures 6.4a and 6.4b that the VN particle mimics the shape of the initial V$_2$O$_5$ particle. The high-magnification SEM image in the inset shows that the VN particle has a porous nature with typical pore sizes below 100 nm.

The second V$_2$O$_5$ precursor contained nanorods (Figure 6.4c). Figure 6.4d shows that this sample was converted into porous nanorods of vanadium nitride. Based on the analysis of SEM data, it can be concluded that the procedure of ammonia reduction of V$_2$O$_5$ precursors leads to the conservation of the overall particles’ shapes.
in the precursor while the interior of particles becomes porous.

These results demonstrate that the selection of a specific morphology of a $\text{V}_2\text{O}_5$ precursor allows one to control the morphology of VN materials produced by NH$_3$ treatment. It is possible to provide a great flexibility in fine tuning the structural details of the materials such as external shape and size of porous particles and their internal morphology. The pseudomorphic reduction by NH$_3$ makes it possible to use the range of available nanomaterials of vanadium oxide (nanotubes, scrolls, nanowires, nanorods and nanoparticles) to produce analogous porous morphologies of VN by the direct conversion of $\text{V}_2\text{O}_5$ materials into vanadium nitrides. The surface area of vanadium nitrides can be tailored since it increases during the conversion. The use of vanadium pentoxide precursors with high surface areas will make it possible to make vanadium nitrides with increased surface areas. This idea is consistent with recent results by Krawiec et al. [199], who obtained vanadium nitrides with surface areas of up to 190 m$^2$ g$^{-1}$ by conversion of a high volume vanadium oxide foam.

The VN materials were also studied by TEM. The sample of single-crystalline nanorods is a particularly convenient precursor to study the structure of VN materials and relate it to the structure of initial $\text{V}_2\text{O}_5$ nanorods. The results of the TEM
study of the sample VN-2 are shown in Figure 6.5. A bright field image of a VN nanorod is shown in Figure 6.5a. The grainy contrast in the image confirms that the nanorod is polycrystalline and consists of a large number of small grains. The SAED diffraction pattern taken from the nanorod is shown in Figure 6.5b. Surprisingly, the pattern resembles that of a single crystal with each spot converted into an arc. Possible explanation to this is that the VN nanorod is a textured polycrystal (with preferential orientation of individual grains) where crystallites inside of the nanorod are slightly rotated in relation to each other. This assumption was proved by analysis of dark-field and high-resolution images of the VN nanorod.

The dark-field image of the nanorod is shown in Figure 6.5c. In order to take the image, the 200 diffracted beam (shown with a circle in Figure 6.5b) was selected. The image shows numerous areas where arrays of grains with similar bright contrast can be observed indicating that corresponding crystallites diffract in a similar manner, i.e. oriented nearly in the same way. Figure 6.5d shows a fragment of the nanorod, revealing grains with pores between them. Figure 6.5e is a high-resolution image taken from the area in Figure 6.5d. Lattice spacings with distances of 0.21 nm (corresponding to the distance between (200) planes of VN) were resolved in two adjacent crystallites. The sets of (200) planes in two crystallites are rotated slightly...
in respect to each other. In order to show this rotation more obviously, an FFT pattern of the high-resolution image in Figure 6.5d is presented in Figure 6.5f. Two pairs of spots can be seen, rotated in relation to each other by a small angle.

The results of dark-field and high resolution studies confirm that $V_2O_5$ materials convert into VN polycrystalline structures with a preferential orientation of grains. The [110] crystallographic direction of VN tends to be parallel to the [010] direction in the initial $V_2O_5$. The nanoscale grains are rotated by a small angle in respect to each other.

The shape conservation and the presence of texture in the samples is potentially beneficial for applications. The structure of porous vanadium nitrides represents a large porous framework where the individual small crystallites are directly connected to each other. The adjacent crystallites have similar orientations with, possibly, only a slightly disordered boundary between them. It is shown in the next chapter of this thesis that such a structure leads to an improved rate capability of VN when it is used as an electrode material for supercapacitors. In other words, porous vanadium nitrides prepared by NH$_3$ reduction of $V_2O_5$ are capable of maintaining a large fraction of their capacitances at high current loads. The NH$_3$ reduction of $V_2O_5$ is a simpler method for producing nanocrystalline porous VN for supercapacitors than the previously suggested method [21, 92]. Although it is also uses NH$_3$ for making VN, the reduction of $V_2O_5$ does not require special equipment such as a glovebox and a glovebag and reduces the number of stages for preparing VN. Unlike the synthesis of VN from VCl$_4$ [21], only one step, heating in ammonia, is required.
Table 6.1: The influence of synthesis parameters on the surface area of vanadium nitride

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Heating rate, °C min⁻¹</th>
<th>NH₃ flow rate, l min⁻¹</th>
<th>Surface area, m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>VN-1</td>
<td>2.8</td>
<td>0.7</td>
<td>22.9</td>
</tr>
<tr>
<td>VN-3</td>
<td>2.8</td>
<td>1.5</td>
<td>29.4</td>
</tr>
<tr>
<td>VN-4</td>
<td>2.8</td>
<td>2.4</td>
<td>32.1</td>
</tr>
<tr>
<td>VN-5</td>
<td>5.1</td>
<td>2.4</td>
<td>29.4</td>
</tr>
<tr>
<td>VN-6</td>
<td>11.2</td>
<td>2.4</td>
<td>26.5</td>
</tr>
</tbody>
</table>

A characteristic pore size distribution of a VN sample obtained at the heating rate of 2.8 °C min⁻¹ and ammonia flow rate of about 0.7 l min⁻¹ is shown in Figure 6.6. The pore distribution is very similar for samples VN-1 and VN-2. It is dominated mostly by pores in the range of 15 - 110 nm (the broad peak on the right hand side of the distribution) but some smaller pores are also present. The measured BET surface areas of the samples VN-1 and VN-2 were 22.9 and 25.4 m² g⁻¹, respectively.

The dependence of the surface area on the synthesis parameters was also studied and is summarized in Table 6.1. In order to evaluate the effect of preparation conditions, a number of VN samples have been prepared from the commercially available V₂O₅ powder. The increase in NH₃ flow rate has a positive influence on the value of the surface area. The surface area increases monotonously with the flow rate. It changes from 22.9 m² g⁻¹ for the flow rate of 0.7 l min⁻¹ to the value of 32.1 m² g⁻¹ for the flow rate of 2.4 l min⁻¹. In contrast, the increase in the heating rate decreases the value of surface area. The surface area diminishes systematically from 32.1 to 26.5 m² g⁻¹ at the high heating rate of 11.2 °C min⁻¹.

The pore size distributions and the dependence of surface area on the synthesis parameters are generally consistent with what can be found in the literature [91, 200] although some differences exist. The pore size distributions of VN catalysts produced by NH₃ reduction of V₂O₅ [200] were found to be similar to those reported here. The pore size distributions of the produced nitrides in that study were narrower for the higher flow rates of NH₃ and the mean pore size decreased. The higher flow rates were found to lead to the increased surface areas of the resulting nitrides, which correlates well with the data presented here.

The dependences of the surface area on the heating rate are different in various studies. It is observed here that the surface area drops monotonously when the heating rate is increased. On the other hand, Kwon et al. [200] reported that the surface area did not change significantly when the heating rate was adjusted between 1 and 3 °C min⁻¹. The value of the surface area remained within the range
of 49 - 59 m² g⁻¹. Kapoor and Oyama [91] reported that the surface area increased with the NH₃ heating rate when the latter was elevated up to 4.8 °C min⁻¹ and decreased at the higher heating rates. At the heating rates higher than 12 °C min⁻¹ the surface area was independent of the heating rate and stabilized at the level of about 60 m² g⁻¹. The surface areas observed in the current study are smaller than some reported values [91, 200], which can be correlated to the fact that vanadium nitrides were prepared using a 'licked' bed of material (the gas flow was passing above the layer of the oxide powder in the furnace tube).

6.4 Conclusions

The application of reduction techniques to the production of nanomaterials of vanadium compounds from vanadium pentoxide has been considered in this chapter. The simple single-step routines of vacuum and NH₃ reduction of V₂O₅ precursors can produce nanomaterials of various vanadium compounds with controlled morphologies including VO₂(B) and V₂O₃ nanorods as well as VN nanorods and porous particles. The reduction techniques have a great potential in converting the large range of available V₂O₅ nanostructured materials (nanorods, nanotubes, porous structures, nanoparticles, and aligned arrays of nanowires on substrates) into the range of corresponding morphologies of nanomaterials of other vanadium oxides (including metastable ones) and vanadium nitride. They provide the way to use the existing synthesis strategies for V₂O₅ nanomaterials to obtain analogous materials of other vanadium compounds by retaining the morphology of precursors.

The produced nanomaterials of vanadium nitride are found to be textured polycrystalline materials. The [110] crystallographic direction of VN materials tends to be parallel to the [010] direction in the initial V₂O₅. The presence of the texture in the polycrystalline compounds of vanadium may provide some advantages for their applications in comparison with conventional randomly oriented polycrystalline materials.
Chapter 7

Electrochemical properties of vanadium nitride

7.1 Introduction

Nanocrystalline vanadium nitride (VN) has been recently proposed as a promising material for pseudocapacitors [21, 92]. It could deliver a specific capacitance of 1340 F g\(^{-1}\) in 1M KOH aqueous electrolyte when a thin film of it (0.25 mg cm\(^{-2}\)) was assessed by cyclic voltammetry at a scan rate of 2 mV s\(^{-1}\). The impressive performance of the material has been attributed to the combination of high metallic electronic conductivity of vanadium nitride and redox reactions provided by few atomic layers of vanadium oxides or oxynitrides on the surface of the material.

Although the material demonstrates attractive electrochemical properties in KOH electrolyte, the properties have not been tested in other aqueous electrolytes. Meanwhile, there are examples of some inorganic materials that exhibit their best performance in other types of aqueous electrolytes. For example, ruthenium oxides are used in acidic (H\(_2\)SO\(_4\)) electrolytes [141], and vanadium oxides provide good performance in neutral electrolytes (such as NaCl and KCl aqueous solutions) [201, 202]. Therefore, VN needs to be further investigated in acidic and neutral solutions since their performance is related to the oxygen-containing layer at the surface and, as a consequence, their electrochemical behaviour may be similar to oxide materials.

A disadvantage of the reported VN materials [21,92] is their limited rate capability. The initially impressive capacitance (at low sweep rates in cyclic voltammetry) was observed to fade considerably when the sweep rate was increased. The effect of material loading, which is possibly related to the poor rate capability, was also reported [92]. Specifically, when the amount of material per unit of area of the current collector was increased, the capacitances were observed to decrease significantly. Only thin films (with densities below 1 mg cm\(^{-2}\)) could deliver attractive capaci-
In this chapter, the electrochemical properties of VN materials produced by temperature-programmed ammonia reduction of V$_2$O$_5$ are assessed in three types of aqueous electrolytes (acidic, alkaline, and neutral). The improved rate capabilities of these textured porous nitrides are demonstrated. The cyclic behavior of vanadium nitrides in 1M H$_2$SO$_4$ and 3M NaCl electrolytes is evaluated and the reasons for changes in electrochemical performance upon cycling are discussed.

### 7.2 Experimental

Vanadium nitrides were prepared by temperature-programmed ammonia reduction of a commercially available V$_2$O$_5$ powder (Sigma-Aldrich) and the preparation procedure is discussed in detail in the previous chapter. After the synthesis, vanadium nitrides were normally passivated with the flowing 0.1% O$_2$ in Ar gas for 2 hours.

Three-electrode cells were assembled to assess electrochemical properties of vanadium nitrides. Two samples of vanadium nitride, VN-1 and VN-4 (prepared at NH$_3$ flow rates of 0.7 and 2.4 l min$^{-1}$, respectively), were evaluated. The working electrode was prepared by mixing VN (80 wt.%), carbon black (10 wt.%) and PVDF (10 wt.%) in NMP (for the sample VN-1) or VN (85 wt.%), carbon black (10 wt.%) and PVDF (5 wt.%) in NMP (for the sample VN-4) and spreading the resulting slurry onto pieces of titanium foil. Pt electrode was used as a counter electrode and Ag/AgCl as a reference electrode. The cyclic voltammetry (CV) and galvanostatic charge/discharge (GC) tests were performed in three electrolytes (3M NaCl, 1M KOH and 1M H$_2$SO$_4$ aqueous solutions). Capacitances were calculated from the discharge branches of galvanostatic charge/discharge curves and areas enclosed by cyclic voltammetry curves.

The initial vanadium nitrides as well as those cycled electrochemically in various electrolytes were characterized by a number of techniques including XRD, TEM and XPS. The binding energy scale in the XPS measurement was corrected for the charging effect by assigning a value of 284.6 eV to the C 1s peak of adventitious carbon. O 1s and V 2p$^3$ lines in the XPS spectra were fitted with several peaks using free XPSPeak 4.1 software. Initial peak positions of 514.1, 515.6, 516.5 and 517.3 eV were used for fitting the V2p$^3$ line (these values correspond to typical positions of the V 2p$^3$ line in VN, V$_2$O$_3$, VO$_2$ and V$_2$O$_5$, see further text for more details). The number of peaks, shapes and positions of them were optimized for the best fit.
7.3 Testing of vanadium nitrides in aqueous electrolytes

7.3.1 Rate capabilities and capacitances

Vanadium nitrides show capacitive properties in all electrolytes. The CV curves of VN-4 in 1M H$_2$SO$_4$, 1M KOH and 3M NaCl aqueous solutions at the sweep rates of 5 and 100 mV s$^{-1}$ are depicted in Figure 7.1. The suitable voltage windows are defined as -0.2 - 0.6 V for 1M H$_2$SO$_4$ and 3M NaCl and -1.2 - 0 V for 1M KOH. The potentials are given versus Ag/AgCl reference electrode. The voltage window of 1.2 V in 1M KOH solution is the same as it was previously reported [21, 92]. All CV curves have a reasonable box-like appearance, and those in 3M NaCl electrolyte (especially at the higher sweep rate) are the closest to the ideal square shape. The ordinate axis in Figure 7.1 represents differential capacitances (specific currents divided by the sweep rates) and such a representation visualizes directly the comparison of capacitances at various sweep rates. It is obvious that VN-4 have attractive rate capabilities since the area enclosed by the CV curve does not fall dramatically when the sweep rate is increased from 5 to 100 mV s$^{-1}$.

![Figure 7.1: CV curves of vanadium nitride (VN-4 sample) in 1M H$_2$SO$_4$ (a), 1M KOH (b) and 3M NaCl (c) aqueous electrolytes at the sweep rates of 5 mV s$^{-1}$ (□, colored) and 100 mV s$^{-1}$ (▽, gray).]
Figure 7.2: Rate capabilities of VN-1. (a, b) Charge/discharge curves at the current loads of 50 mA g$^{-1}$ and 1 A g$^{-1}$, respectively. (c) Capacitance retention at various current loads. Red curves correspond to 1M H$_2$SO$_4$ electrolyte and green curves correspond to 3M NaCl electrolyte.

Figure 7.2a,b shows the charge/discharge curves of VN-1 in 1M H$_2$SO$_4$ and 3M NaCl electrolytes at the current loads of 50 mA g$^{-1}$ and 1 A g$^{-1}$. The curves show a triangular shape close to an ideal one at both current rates and only a minor IR drop is detected in the GC curves when the current of 1 A g$^{-1}$ is switched to the opposite value. The time of charge and discharge is longer in 1M H$_2$SO$_4$ solution since vanadium nitride demonstrates higher capacitances in this electrolyte. The capacitance retention of VN-1 at different current loads is depicted in Figure 7.2c. Overall, VN-1 shows attractive rate capabilities. When it is charged and discharged at the current load of 1 A g$^{-1}$, it demonstrates 79% of the capacitance measured at 50 mA g$^{-1}$ in 1M H$_2$SO$_4$ solution and 84% of the initial capacitance in 3M NaCl electrolyte.

Choi et al. [92] indicated that the performance of vanadium nitrides in 1M KOH was dependent strongly on the material density on the current collector. When the material loading per unit of area of the current collector was increased, the capacitance of VN dropped and rate capabilities degraded noticeably. For example, the capacitance of vanadium nitride with the density of 0.99 mg cm$^{-2}$ was almost twice smaller than that of VN with the density of 0.25 mg cm$^{-2}$ at the CV scan rate.
of 2 mV s\(^{-1}\) and became 5 times smaller at the sweep rate of 100 mV s\(^{-1}\).

In the present study, vanadium nitrides are prepared by a different approach, NH\(_3\) reduction of V\(_2\)O\(_5\), and the dependence of the capacitances and rate capabilities on the material loading is weak and does not demonstrate a dramatic decrease with the increase in the material’s density. For example, electrodes with densitites of 1.1 and 0.55 mg cm\(^{-2}\) demonstrated similar capacitances in 1M KOH (101 and 105 F g\(^{-1}\) at the CV sweep rate of 5 mV s\(^{-1}\)). Furthermore, the vanadium nitrides in this study can retain impressive rate capabilities even at high material loadings on a current collector. The rate capabilities shown in Figure 7.2, for example, were measured using thick films of VN (with densities of about 4 - 6 mg cm\(^{-2}\)).

A better rate capability and weak dependence of the capacitance on material loading can be correlated with the structure of vanadium nitrides produced by NH\(_3\) reduction of V\(_2\)O\(_5\). It is demonstrated in the previous chapter that VN materials produced by this approach are porous microparticles composed of nanocrystalline grains that are directly attached to each other. In other words, such a structure represents a large porous framework and the individual small crystallites within this framework are directly connected. The electronic conductivity of vanadium nitride is metallic (\(\sigma_{\text{bulk}} = 1.67 \times 10^6 \ \Omega^{-1}m^{-1}\), as it is given in [92]) and we can anticipate that the porous crystalline frameworks of this material would provide an attractive conductivity. It is also shown in chapter 6 that the polycrystalline particles are textured, i.e. the adjacent crystallites have similar orientations with, possibly, only a slightly disordered boundary between them. This factor may also contribute to the improved conductivity of the porous polycrystalline material. Overall, the specific structure of vanadium nitrides produced by reduction of V\(_2\)O\(_5\) seems to play a crucial role for the capacitance retention at higher sweep rates or current loads.

The amount of oxygen at the surface of vanadium nitride is an important parameter affecting the capacitance of the material. Figure 7.3 shows capacitances of three identical samples of VN-1 (different only in the post-treatment oxidation procedure) in three electrolytes. The first sample is exposed to air after cooling down in the NH\(_3\) flow and purging the tube with N\(_2\) flow for 2 hours. The second sample is passivated with flowing 0.1 % O\(_2\) in Ar gas after cooling down in NH\(_3\) and the third sample is passivated with 0.1 % O\(_2\) in Ar first and subsequently annealed in air at about 200 °C for 2 hours. Different approaches to the surface oxidation of VN have a clear effect on the capacitances of VN-1. The samples with oxidation performed in a controlled way (in 0.1 % O\(_2\) in Ar) have up to two times higher capacitances in all electrolytes than the sample exposed to air directly after synthesis. The capacitance of VN-1 in 1M KOH can be further improved after additional annealing in air at 200 °C while that in 3M NaCl electrolyte decreases after such a procedure. The
capacitance in 1M H$_2$SO$_4$ solution also decreases slightly after additional annealing.

The highest value of capacitance was achieved in 1M KOH electrolyte for VN-1 coating with a density of 0.7 mg cm$^{-1}$ after its passivation with 0.1 % O$_2$ in Ar gas (■), passivation with 0.1 % O$_2$ in Ar gas (▽), the same passivation procedure followed by annealing in air at 200 °C (□).

X-ray photoelectron spectroscopy is an effective tool to study the composition of a surface layer of materials (2 - 4 nm in depth). It allows one to determine the presence of elements at the surface, estimate their content quantitatively and, in some cases, study the depth profile of elemental composition at the surface of the samples [203]. If a particular element exhibits different oxidation states, the XPS technique is capable of distinguishing between them. A great care, however, has to
be exercised to determine the presence of vanadium in different oxidation states since
the binding energies (BE) of V 2p$^3$ line (which is normally used) for vanadium oxides
with various oxidation states of vanadium (V$_2$O$_5$, VO$_2$, and V$_2$O$_3$, corresponding
to V$^{5+}$, V$^{4+}$, and V$^{3+}$) is in a narrow range of about 515.5 - 517.5 eV [204]. The
situation is further complicated since a range of BE values is reported for each
oxidation state of vanadium possibly due to equipment calibration differences and
inaccuracy of the correction for sample charging [205].

Bondarenka et al. [205] conducted a useful statistical analysis of XPS literature
data on the binding energies of V 2p$^3$ lines for vanadium in different oxidation
states. The reported binding energies for V$^{5+}$, V$^{4+}$ and V$^{3+}$ species were found to
correspond to three Gaussian distributions centered at 517.3, 516.5 and 515.6 eV,
respectively, with the statistical deviation $W_{BE} = 0.25$ eV. In other words, the re-
ported binding energies for V$^{5+}$, V$^{4+}$ and V$^{3+}$ species are in the ranges 517.3 ± 0.25,
516.5 ± 0.25 and 515.6 ± 0.25 eV with a probability of 70% and within the ranges
517.3 ± 0.5, 516.5 ± 0.5 and 515.6 ± 0.5 eV with a probability of 95 % [205]. A
careful data analysis is therefore possible for the reliable qualitative separation of
vanadium species in different oxidation states.

The XPS spectrum of VN-4 passivated with 0.1 % O$_2$ in Ar gas is shown in
Figure 7.4. A clear O 1s line confirms that a thin oxide layer exists on the surface
of VN. The oxygen signal is fitted with two peaks. The main component is centered
at 530.3 eV and is typical for oxygen in a metal oxide. The second small peak is at
about 531.8 eV and can be attributed to the signal from -OH groups chemisorbed
at the surface. The BE of such a feature is typically 1.3 - 1.6 eV higher than that of an oxide in an XPS spectrum. The V 2p \(^3\) line was fitted with three peaks. The peak at 513.9 eV belongs to vanadium in the vanadium nitride structure. Two other features composing the V 2p \(^3\) line are centered at 515.0 and 517.2 eV and, most likely, correspond to V\(^{3+}\) and V\(^{5+}\) oxidation states of vanadium in surface oxides. The composition of the surface oxides is different from that in the previous study [92] where the V 2p \(^3\) line was a combination of the nitride peak at 514.1 eV and the second feature centered at 516.3 eV. The latter is likely to be related to the V\(^{4+}\) oxidation state of vanadium. The value 516.3 eV fits well into the typical range of binding energies for V\(^{4+}\) (515.6 ± 0.5 eV [205]).

The passivation with an inert gas containing a small amount of O\(_2\) (0.1 - 2 %) is an established procedure for VN materials in the field of catalysis [91, 199, 200]. It is considered capable of preventing excessive oxidation of nitride by introducing a very thin layer of protective oxide on the surface. Choi et al. used this approach (particularly, a gas mixture of 0.1 % O\(_2\) in Ar) for passivation of VN supercapacitors and achieved high capacitances [92]. The same procedure is intentionally applied in this study to control the surface functionalities of vanadium nitrides. However, according to the XPS data and lower values of capacitances achieved, the composition of the surface layer of VN is different. The V\(^{5+}\) and V\(^{3+}\) states are dominant at the surface of nitride in the current study while V\(^{4+}\) is the most likely oxidation state observed for vanadium in the previous publication [92]. The use of inert gases with low oxygen admixtures cannot be regarded as a reliable procedure to introduce the necessary functionality capable of providing high capacitances in vanadium nitrides. Further research is needed in order to find reliable methods to control the surface composition of vanadium nitrides and their capacitive properties. The surface chemistry can be sensitive to a number of parameters such as the temperature of passivation, oxygen content in the gas, surface area and pore structure of a nitride as well as the presence of additional annealing.

The vanadium nitrides reported in this study have advanced rate capabilities. It is believed that a targeted study of techniques for surface chemistry modification will allow one to obtain the material combining high capacitances with attractive rate capabilities.
7.3.2 Cyclic behavior

This section reports the study of the cyclic behavior of vanadium nitrides. The cyclic behaviour of VN in 1M KOH has been studied previously by Choi et al. [92] and the attention here is given to other electrolytes, 1M H₂SO₄ and 3M NaCl. In the case of KOH solution, it was found by CV experiments [92] that a stable cycling for up to 1000 cycles can be achieved by narrowing down the voltage window to 0.9 V and adjusting pH of the solution from 14 to 12.

Figure 7.5 shows the cyclic behavior of VN-1 and VN-4 in the course of 1000 cycles of galvanostatic charging and discharging at the current load of 500 mA g⁻¹ in 1M H₂SO₄ electrolyte. Both samples lose most of their capacitances over the first 200 - 300 cycles and the further slow capacitance drop is also evident. VN-1 loses its capacitance at a higher rate over the first 200 cycles. The stabilized capacitance after 1000 cycles is about 5 - 7 F g⁻¹ and is almost the same for both samples. To sum up, vanadium nitrides are found to lose their capacitance over the first 300 cycles upon their galvanostatic charging and discharging in 1M H₂SO₄ solution.

The electrode materials after cycling were studied by XRD and the corresponding patterns are shown in Figure 7.6. The pattern of the electrode material containing VN-1 (Figure 7.6a) shows a family of vanadium nitride reflections. It is difficult to judge reliably if some significant structural changes happened since the same crystalline peaks are observed in the fresh VN materials. On the other hand, the presence of structural changes in the electrode is evident from Figure 7.6b (the XRD pattern of VN-4 electrode after cycling). The vanadium nitride peaks in this material have suppressed intensities and reflections with weak relative intensities (such as (311) and (222)) cannot be found in the pattern anymore. The possible explanation is that the amount of crystalline vanadium nitride decreased significantly in this sample.

In order to obtain a further insight into what happened to VN-4 material after cycling, a TEM study was conducted. Figure 7.7 shows the results of the TEM investigation of the VN-4 electrode after 1000 galvanostatic charge/discharge cycles in 1M H₂SO₄. As it can be seen from Figure 7.7a, a typical fragment of the electrode is an agglomerate of small particles. The particles give only a weak contrast in the bright-field TEM image (i.e. diffract electrons from the central beam weakly), which can be related to their poor crystallinity. The SAED pattern taken from the agglomerate (Figure 7.7b) shows only weak diffuse rings typical for amorphous materials. A very limited number of crystalline reflections (shown with arrows) related to vanadium nitride can be observed. XEDS spectrum collected from the agglomerate (not shown) is dominated by a strong carbon-related peak. The high-resolution image in Figure 7.7c demonstrates representative nanoparticles in the agglomerate
Figure 7.5: Cyclic behavior of VN-1 (□) and VN-4 (■) in 1M H$_2$SO$_4$ at the current load of 500 mA g$^{-1}$ up to 1000 GC cycles.

Figure 7.6: XRD patterns of VN-based electrodes after 1000 GC cycles in 1M H$_2$SO$_4$ electrolyte. (a) Electrode material with VN-1 active component. (b) Electrode material with VN-4 active component.
with a structure typical for poorly graphitized carbons. Based on the TEM results, it can be concluded that most of the active material, vanadium nitride, is removed from the electrode and the material after cycling consist mainly of carbon black used for the assembly of the electrode and a small quantity of residual vanadium nitride.

It follows from the results of XRD and TEM analyses that the capacitance drop observed in the cyclic behavior of vanadium nitrides subjected to galvanostatic charging and discharging in 1 M H$_2$SO$_4$ is most likely associated with gradual dissolution of vanadium nitride in the acidic medium. The dissolution effect after 1000 cycles is particularly pronounced in the electrode with VN-4 active component, where only some residual VN crystallites are left and most of the electrode material after cycling consists of carbon particles used as an additive for the assembly of the electrode.
Figure 7.8: Cyclic behavior of VN-4 in 1M H$_2$SO$_4$ at the sweep rate of 50 mV s$^{-1}$ up to 100 CV cycles.

Figure 7.9: XPS spectrum of VN-4 after 100 cyclic voltammetry cycles in 1M H$_2$SO$_4$ electrolyte.
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It is important to note that the cycling behavior of vanadium nitride is quite different when it is subjected to periodic potential changes (cyclic voltammetry). Figure 7.8 shows the capacitance of VN-4 during 100 CV cycles in 1M H$_2$SO$_4$ at the sweep rate of 50 mV s$^{-1}$. The initial small capacitance drop from 58 to 47 F g$^{-1}$ is followed by a stable performance of vanadium nitride for another 90 cycles. Unlike the case of GC cycling, the quick decrease of the capacitance is not observed.

The results of an XPS analysis of VN-4 material after 100 cyclic voltammetry cycles are shown in Figure 7.9. The V 2p$^3$ line can be fitted with three components. The peak at 513.9 eV relates to vanadium in the nitride and the position of this peak is the same as that of the corresponding peak of the as-produced VN-4 (Figure 7.4). Two other features composing the V 2p$^3$ line are centered at 514.9 and 516.8 eV and can be attributed to V$^{3+}$ and V$^{4+}$ signals. The presence of V$^{4+}$ and disappearance of V$^{5+}$ species indicate certain reduction of vanadium in the surface oxygen-containing layer. The O 1s peak after 100 cycles can be deconvoluted into 3 components. The intensity of the peak centered at 531.8 eV is enhanced possibly due to the presence of a large number of -OH groups at the surface. The third feature at 533.2 eV may appear due to oxygen combined with the adventitious carbon (i.e. C-OH structures) and, if it is the case, is an artefact. On the other hand, the peak at about 533 eV was attributed in some studies to the signal from H$_2$O in hydrated vanadium oxides [206]. It is difficult to judge reliably about the nature of this signal. The detected changes in the surface layer of VN are consistent with the initial quick decrease in the capacitance of VN-4 when it undergoes cyclic voltammetry (Figure 7.8). The changes in the surface composition must have happened quickly (during the first few cycles) since the observed capacitance was stable during the following 90 cycles.

The experimental data suggest that the cycling stability of vanadium nitrides can vary if the material is subjected to different electrochemical procedures, particularly to galvanostatic charging/discharging and cyclic voltammetry. Generally, vanadium nitride enjoys having a reputation of a material with a high chemical stability [92,207]. The stability of micro-sized VN in H$_2$SO$_4$ solutions was previously assessed at 95 °C by Lyutaya and Kulik [208] and no signs of noticeable dissolution were detected after 1 h of treatment. In this study, VN keeps a good stability when it is subjected to cyclic voltammetry while it tends to dissolve in H$_2$SO$_4$ solution upon galvanostatic charging and discharging. The material’s stability depends clearly on the type of the electrochemical stimulation. The dissolution of VN in H$_2$SO$_4$ can be also favoured by a nanoscale size of individual particles composing the porous VN frameworks (i.e. by an increased surface area of VN in comparison with micro-sized particles).
Figure 7.10: Cyclic behavior of VN-1 (□) and VN-4 (■) in 3M NaCl at the current load of 500 mA g\(^{-1}\) up to 1000 GC cycles.

VN materials show interesting changes in capacitance upon cycling in 3M NaCl solution. Figure 7.10 shows the capacitance versus cycle number during galvanostatic charging and discharging at 500 mA g\(^{-1}\) up to 1000 cycles. It can be seen that a gradual activation of the material happens upon cycling leading to the increased capacitance. Two samples studied exhibit different behaviors. VN-1 reaches a maximal capacitance of about 175 F g\(^{-1}\) after 300 cycles and the capacitance gradually decreases afterwards. VN-4 benefits from the increasing capacitance over the whole range of 1000 cycles. The initial modest capacitance of 33 F g\(^{-1}\) increases monotonously up to a value of 146 F g\(^{-1}\), showing a capacitance which is 4.5 times larger than the initial value. The observed differences may relate to a value of the surface area of this materials and the differences in surface oxide structures between them.

Figure 7.11 shows the results of XPS characterization of VN-4 after 100 galvanostatic charge/discharge cycles in 3M NaCl electrolyte. It is obvious that the oxide component of the V 2p\(^3\) line gets much more pronounced than that in the initial nitride material while the nitride component of the V 2p\(^3\) vanishes. The line is fitted with three peaks, and the peak centered at 517.1 eV (related, most likely, to V\(^{5+}\)) dominates. The observed changes in the intensities of the components suggest that the nitride undergoes oxidation upon cycling in NaCl solution. The relative intensity of the O 1s peak increases as well, supporting the idea about gradual oxidation of vanadium nitride. The XPS measurement also detected the presence of sodium.
Figure 7.11: XPS spectrum of VN-4 after 100 galvanostatic charge/discharge cycles in 3M NaCl electrolyte.

Figure 7.12: XRD patterns of VN-based electrodes after 1000 GC cycles in 3M NaCl electrolyte. (a) Electrode material with VN-1 active component. (b) Electrode material with VN-4 active component.
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(\(Na\) 1s line) in the surface layer of vanadium nitride after 100 cycles in NaCl.

Figure 7.12 shows XRD patterns of VN-based electrodes after galvanostatic cycling in 3M NaCl electrolyte. Both patterns show the reflections related to the VN phase. In addition, a new diffraction peak is observed at the position of about 59 - 60 degrees. This peak has a higher relative intensity than the most intense peaks of VN in the pattern of VN-1 (Figure 7.12) while its intensity is smaller than that of strong peaks of vanadium nitride in the case of VN-4. Additional weak hills not related to vanadium nitride phase are observed between 30 and 40 degrees in the diffraction pattern of VN-1. The new features in the XRD patterns are shown with arrows in Figure 7.12. Unfortunately, the low amount of material available did not allow us to obtain a clear diffraction pattern with better signal-to-noise ratio. The data obtained by XRD indicate that a new phase is formed in the electrode materials and the relative amount of this phase is higher in the case of VN-1. It is likely, therefore, that the observed changes in the capacitance of vanadium nitride upon cycling are related to the formation of new electrochemically active phase in the material.

Further careful investigation is needed to identify the nature of changes in the VN material. It is clear at this stage that a new phase forms after prolonged cycling. This phase is related to the gradual oxidation and incorporation of sodium detected by XPS. The electrochemical performance of two VN samples after 1000 cycles is different and can be correlated with the relative amounts of the new phase and VN in the electrodes. Certain proportion of two phases leads to an enhanced capacitance while the excessive formation of the new phase is not beneficial.

7.4 Conclusions

The electrochemical properties of vanadium nitrides synthesized by temperature-programmed \(\text{NH}_3\) reduction of \(\text{V}_2\text{O}_5\) are assessed in three aqueous electrolytes (1M \(\text{H}_2\text{SO}_4\), 1M KOH and 3M NaCl). The materials show capacitive properties in all electrolytes. The VN sample synthesized by this approach are capable of providing attractive rate capabilities. Vanadium nitrides can retain about 80% of their capacitance (measured at 50 mA g\(^{-1}\)) at a high current load of 1 A g\(^{-1}\). The capacitances of vanadium nitrides are sensitive to the composition of the surface oxide layer and further research is needed to find a reliable way to introduce the optimal surface functionalities on the nitride surfaces.

The cyclability tests show that the chemical stability of VN in the acidic electrolyte depends on the method of its electrochemical stimulation. The nitride is stable in a cyclic voltammetry test but tends to dissolve in 1M \(\text{H}_2\text{SO}_4\) solution
when it is charged and discharged galvanostatically. The galvanostatic charging and discharging of VN in 3M NaCl electrolyte leads to its electrochemical activation caused by the formation of a new phase in the electrode. The new phase is likely to be related to the gradual oxidation and incorporation of sodium detected by XPS.
Applications of ball milling to the synthesis of nanomaterials of zinc oxide and vanadium compounds have been studied. The mass synthesis of V$_2$O$_5$ nanomaterials is a particularly important issue since it opens pathways to the preparation of analogous morphologies of other vanadium compounds via reduction techniques. The nanomaterials obtained have useful optical and electrochemical properties.

In the case of ZnO, ball milling affects the evaporation behavior of the material. The milled ZnO tends to evaporate faster than a conventional untreated powder. A larger amount of the vapor generated upon annealing can be used for the growth of nanowires. Although some moderate advances in the quantity of nanowires can be possibly achieved, the basis process remains relatively inefficient, with little promise of extension to any real large scale production (grams and kilograms) of ZnO nanowires. On the other hand, the larger amount of vapor may trigger the formation of some unusual morphologies of nanomaterials, such as nanowires with corrugated surfaces.

Ball milling and annealing is a much more promising procedure for the mass production of nanomaterials of V$_2$O$_5$. V$_2$O$_5$ has a pronounced layered structure with weak bonding between layers and, as a consequence, the surface energy of {001} planes is much lower than the surface energies of other possible planes. The ball milled V$_2$O$_5$ powder tends to recrystallize into V$_2$O$_5$ nanorods dominated by {001} crystal surfaces. In addition, vanadium pentoxide has a moderate melting point (690 °C) and bulk recrystallization can be achieved at reasonable temperatures due to active surface diffusion.

To achieve a real large scale synthesis, the problem of excessive sintering must be resolved. When the milled V$_2$O$_5$ powder is annealed as a static layer, it tends to aggregate into a large polycrystalline brick. A possible solution may be found by carrying out the annealing in a fluidized bed. Under these conditions the particles are suspended in air and sintering is minimized. To test this idea 1 g of V$_2$O$_5$ powder was
annealed in a vertically vibrated reactor. After the annealing the sample of V\(_2\)O\(_5\) nanorods stayed in powder form and the agglomeration was indeed successfully suppressed. The combination of ball milling and annealing in a fluidized bed would therefore appear to be a promising method for large-scale nanorod production. Both processes are scalable. Large commercial mechanical mills are available and fluidized bed reactors are already used in a variety of industrial applications.

An additional attractive aspect of the large scale synthesis of V\(_2\)O\(_5\) nanomaterials lies in the ease of conversion into a number of other vanadium compounds by reduction techniques. Typically, vanadium compounds with the oxidation state of vanadium lower than 5+ have high melting points and the solid-state pseudomorphic conversion of V\(_2\)O\(_5\) into these phases is clearly possible. The nanomaterials produced can be textured, i.e. can retain a preferential orientation of individual grains dictated by the crystalline orientation of the V\(_2\)O\(_5\) precursor. Such a transformation of V\(_2\)O\(_5\) nanorods into nanorods of VO\(_2\), V\(_2\)O\(_3\) and VN has been described in this thesis. The clear presence of texture - preferential crystal orientation - has been unambiguously demonstrated for VN.

The properties of nanomaterials relate directly to their future applications and are therefore of central importance. It is for this reason that the optical (luminescent) properties of ZnO nanowires have been studied, and is also why the properties of V\(_2\)O\(_5\) and VN materials related to their applications in batteries and supercapacitors have been tested. Particular emphasis has been given to the very promising electrochemical properties of vanadium compounds.

V\(_2\)O\(_5\) nanorods with a suppressed thickness along the [001] crystallographic direction have an advanced cycling stability for lithium intercalation. They can retain a stable capacity of about 260 mAh g\(^{-1}\) upon cycling. This is a clear advantage over many current V\(_2\)O\(_5\) materials which lose their capacity during cycling. At present most publications related to lithium batteries ignore the importance of crystal orientation and focus only on the influence of particle size. The beneficial properties of the single-crystalline V\(_2\)O\(_5\) nanorods are a good example of the importance of crystal orientation for the intercalation of guest species.

Polycrystalline vanadium nitrides synthesized by the reduction of V\(_2\)O\(_5\) have attractive rate capabilities. At a high current load of 1 A g\(^{-1}\) VN can retain about 80% of its capacitance demonstrated at the current load of 50 mA g\(^{-1}\). VN exhibit capacitive properties in each of three types of electrolytes tested (1M KOH, 1M H\(_2\)SO\(_4\) and 3M NaCl). The cyclability of VN in 1M H\(_2\)SO\(_4\) and 3M NaCl electrolytes has been checked, and an interesting activation mechanism via formation of a new phase is observed in the latter electrolyte.
The research presented in this thesis opens promising new directions for future studies. It is anticipated that the method of large-scale synthesis demonstrated for V$_2$O$_5$ nanorods can be extended to nanorods of other phases. Likely candidates include phases consisting of weakly bonded layers and possessing moderate melting points. A very obvious candidate is MoO$_3$, another orthorhombic material with a moderate melting point. It is famous for its belt-like morphologies, which are used for calibration of the rotation of diffraction patterns in transmission electron microscopy. Other promising phases can be found in the coupled analysis of thermal stability and crystal structures of materials. Calculation of surface energies can also be a useful tool for finding suitable materials.

Pseudomorphic reduction can yield a large number of phases of compounds of vanadium, particularly oxides. It has been demonstrated that V$_2$O$_5$ can be converted to VO$_2$(B), V$_2$O$_3$ and VN. The transformation to VN, in particular, takes place via a number of intermediate phases. Kwon et al. [200] proposed that the reduction of V$_2$O$_5$ happened in a sequential transformation V$_2$O$_5$ $\rightarrow$ V$_4$O$_9$ $\rightarrow$ VO$_2$ $\rightarrow$ V$_2$O$_3$ $\rightarrow$ VO$_{0.9}$ $\rightarrow$ VN, whilst Kapoor and Oyama suggested a different reaction pathway V$_2$O$_5$ $\rightarrow$ V$_6$O$_{13}$ $\rightarrow$ V$_2$O$_4$ $\rightarrow$ VO$_2$ $\rightarrow$ V$_2$O$_3$ $\rightarrow$ VO $\rightarrow$ VN [91]. In either event intermediate phases such as V$_4$O$_9$, V$_6$O$_{13}$ and VO can almost certainly be isolated by arresting the reduction process at the appropriate time. The resulting VN materials studied in this thesis demonstrate the presence of preferential grain orientation. The texture is to be expected for all intermediate phases.

Transition metal nitrides represent a new type of materials for applications in supercapacitors. Many of them possess a high metallic conductivity combined with the presence of oxide structures on the surface. Such a core-shell composite is potentially promising for the application in supercapacitors since the nitride core provides high conductivity and the oxide overlayers participate in the capacitive mechanism. Interestingly, nitrides have not yet been the object of much research attention and only a limited number of reports can be found in the literature for VN [21,92], Mo$_x$N [209] and TiN [210]. A focused study of transition metal nitrides can possibly discover attractive new materials for high-performance electrodes of supercapacitors.
References


