3 Scope and Objectives

The search for novel methods to synthesize nano-objects with controlled shape, size, and composition still remains a challenge. In this class of nano materials, especially nano particles with a tubular morphology are very attractive because of their large anisotropy and geometrical pre-functionalization (**Fig. 3.1**).

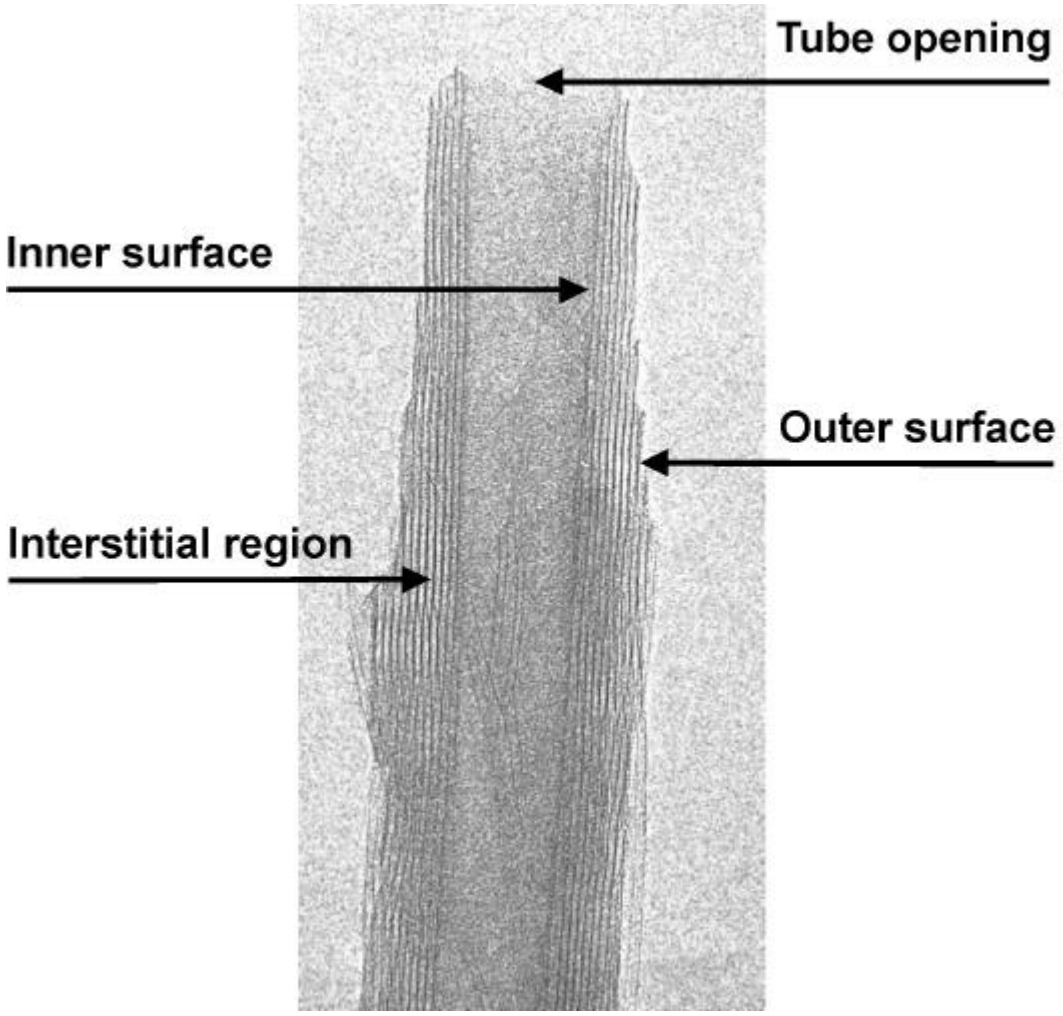

Fig. 3.1: The four topologically different functional sites of vanadium oxide nanotubes [1].

In 1991, Iijima reported the preparation of a new type of carbon structure, consisting of needle-like tubes with graphitic sheets [2]. The number of layers varied from 2 to 50.

The outer diameters of the carbon nanotubes ranged from 4 to 30 nm and they were up to 1 µm in length. Two years later, in 1993, the synthesis of single-walled nanotubes was presented [3,4]. These tubules showed diameters of 0.7 to 1.6 nm, with a length of less than 1 µm. Although many different synthesis procedures were developed like arc-discharge techniques [5-7], thermal decomposition of benzene [8] and acetylene [9], laser vaporization of graphite rods [10-12], disproportionation of carbon monoxide [13,14], or electrolysis in molten alkali halide salts using carbon electrodes [15,16], carbon nanotubes are still not available at low cost in large quantities.

In general, all compounds with graphite-analogue layered structures should be able to form nanotubes or fullerene-type structures [17]. The similarity of MoS_2 and its analogues of transition metal chalcogenides to graphite provides the capability to form closed fullerene-type structures [18], as well as nano- and microtubes [19-24]. But curved structures are not limited to carbon and molybdenum or tungsten sulfide. Long known prototypes of tube-like structures are silicate minerals like chrysotile $Mg_3(OH)_4[Si_2O_5]$ [25]. In this case, the inner diameter is about 5 nm, the outer diameter 20 nm. In contrast to the layered materials mentioned above, the synthesis of titanium oxide nanotubes (anatase phase) with inner diameters of about 5 nm and outer diameters of about 8 nm and a length of about 100 nm was reported [26,27] recently.

With the discovery of the vanadium oxide nanotubes (VO_x-NTs) in our group [28,29], the question was raised whether it may be possible to synthesize other transition metal oxide nanotubes by a similar route. Most promising materials for the development of tubelike nano particles seem to be layered transition metal oxides like V_2O_5 or MoO_3. Consequently, our preferred method for the synthesis of nanostructured transition metal oxides involved template-directed sol-gel procedures, followed by hydrothermal treatment.

Although many experiments were performed, it was not possible to synthesize a further transition metal oxide in a tubular morphology in this work, however. A large set of new and surprising morphologies have been found, either with intercalated template molecules or without. These shapes include fibers, cubes, discs, spheres, rods or lamellar inorganic-organic composites.

The role of chemistry within materials science has been discussed in **Chapter 1**. In addition, a few new aspects in solid state chemistry and a short overview of the chemistry in the nanometer regime are given with some further definitions and possible applications.

Chapter 2 has resumed pioneering work in the template-directed synthesis of structured materials. An overview of the literature on the preparation of structured transition metal oxides is given.

The experimental part is presented in **Chapter 4**.

Chapter 5 deals with the synthesis of VO_x-NTs and their topochemical reactions. In addition to the well-known alkoxide route to VO_x-NTs [30,31], a novel large-scale synthesis procedure has been developed applying either $VOCl_3$, HVO_3 or V_2O_5 as vanadium source [32]. Due to the low cost and ease of handling, especially the synthesis starting from V_2O_5 provides an advantageous access to large quantities of the novel tubular material [33]. The highly flexible scroll-like structure [34] of the tubes allows for the substitution of the intercalated templates by diamines [35] and metal cations [36,37], while the tubular morphology is preserved.

Chapter 6 reports experiments with molybdenum oxide. The reaction of molybdic acid in presence of long-chain primary amines, followed by hydrothermal treatment, led to a lamellar molybdenum oxide-amine composite. Removal of the intercalated amines by reaction with nitric acid yielded a template-free molybdenum oxide phase with a fibrous morphology in the nanometer regime [38,39].

Structured iron oxides are presented in **Chapter 7**. A simple procedure is described for the synthesis of monodispersed colloidal iron oxide particles involving the use of a soluble and hydrolyzable hexanuclear iron(III) polyolate complex as precursor instead of inorganic salts [40]. The composition, size, and shape of the particles was controlled by the addition of various neutral and charged organic surfactants and by adjusting reaction conditions like aging time and temperature. In addition to the polyolate complex, also the hydrolysis of iron(III) alkoxides in presence of organic additives was investigated. But the time-consuming synthesis of the alkoxides probably prevents an industrial application of these compounds as iron oxide precursors.

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