Volume 5

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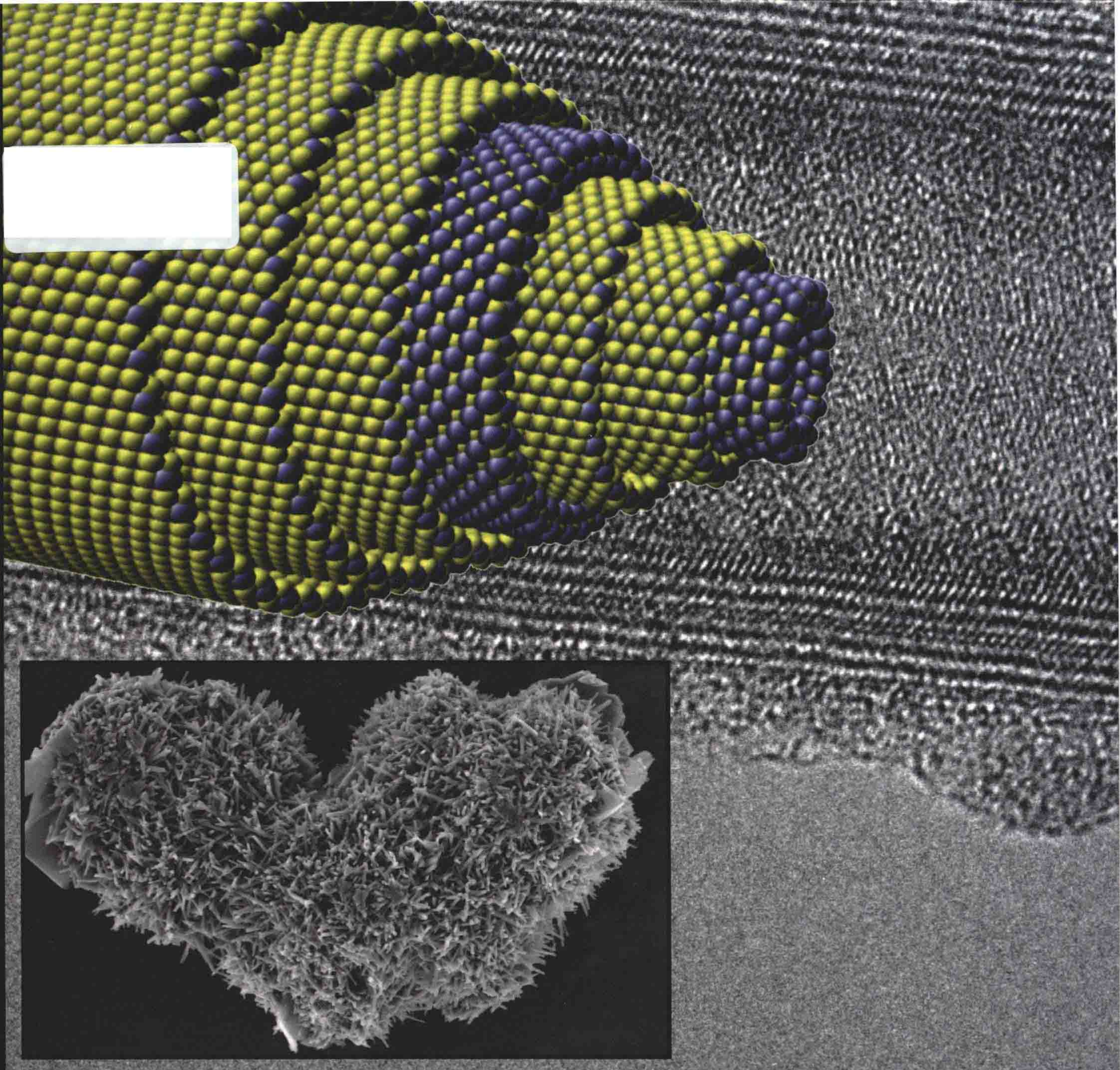

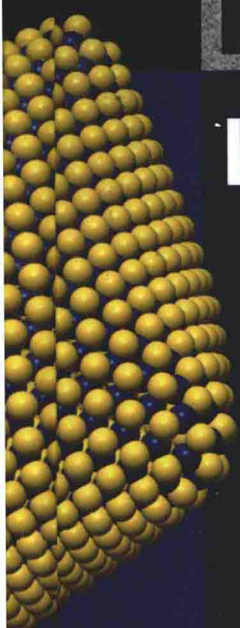

Inorganic Nanomaterials from Nanotubes to Fullerene-like Nanoparticles

Fundamentals and Applications

Reshef Tenne

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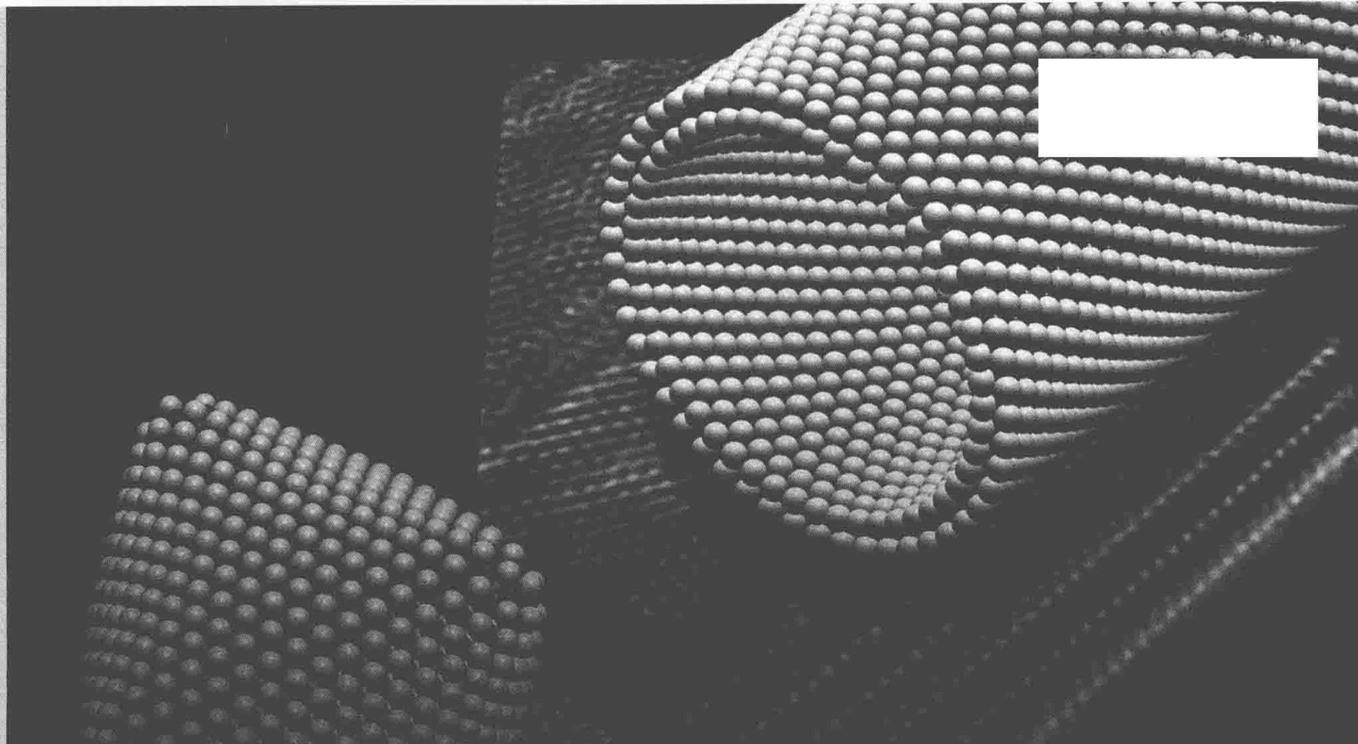

Image courtesy of Dr. Maya Bar-Sadan

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FOREWORD

After 20 years of intensive research on the topic of inorganic nanotubes (INT) and fullerene-like (IF) structures, I feel that the time is ripe for me to look back and reflect on the accomplishments and also the failures and errors which were committed along the way. During this period we published some 200 publications in various forms, and the field has evolved from a scientific curiosity to a discipline of its own. The fact that on top of the curiosity-driven science we were able to advance numerous applications is especially gratifying. Regrettably, the commercialization of the products based on this research is progressing slowly.

I feel fortunate to be at the Weizmann Institute, where the scientific environment allows me to pursue this line of research in complete freedom and with a great deal of support and encouragement. This feeling of mutual commitment was particularly important at times that my focus was on the health of my late wife Lea and conditions were far from optimal to produce first rate data.

I am grateful to my students and research associates who showed a sense of commitment to the field, and worked diligently to make this work flourish. Many of my students and some associates came to Israel with the wave of immigration from the former Soviet Union. While supervising them academically towards higher degrees, I was also involved in helping them surmount great difficulties in resettling and establishing their life in a new country. In return they showed great affection to me personally and to the research work, and I am grateful to them, as well as to all my students and research associates.

One important lesson that I have learned in my career is the value of collaborations. Probably 80% of my publications were accomplished in the context of different collaborations. Some of the collaborations were a result of an exchange of ideas in the corridor. Others came about after a chance encounter at a conference, while a few collaborations were highly planned. Still other collaborations occurred after joining a consortium funded by a research agency. Irrespective of the reason, I learned that two of the most important ingredients for a successful collaboration are the complementarity of the research interest among the partners, and the ability to share credit. I am genuinely grateful to all my collaborators from whom I learned so much, and who have enriched my knowledge and experience in so many ways.

I hope the reader will find the book interesting, and will be able to share the great enthusiasm that I experience almost daily as I examine an electron microscope image of a new nanotube — just synthesized by one of my students.

CONTENTS

Characterization

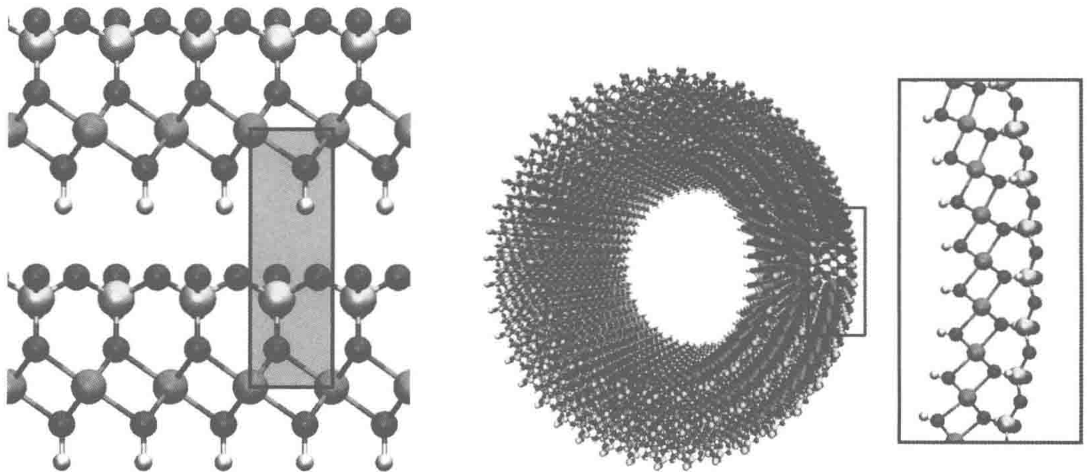
Application

GENERAL INTRODUCTION

The present book is a judicious assembly of some 45 of the most important publications of Prof. R. Tenne from his work over the last two decades. These publications are focused on the study of closed-cage and hollow nanostructures from inorganic compounds with layered (2-D) structure. These nanostructures come generally as multiwall quasi-spherical nanoparticles- the so-called inorganic fullerene-like (IF) or as inorganic nanotubes (INT). As such they may be considered as the extension of the well-known carbon fullerenes and carbon nanotubes. Before going into a detailed discussion of the virtues of this new class of materials, a short background into the discipline of hollow nanostructures is desirable.

The chemical bond is unstable beyond a distance of 2–2.5 Å and even weak chemical forces, such as the van der Waals or hydrophobic interactions become insignificant beyond 5–7 Å. Generally speaking, therefore, chemistry is not favorable to open spaces and hence most crystalline materials are compact and do not contain voids or hollow space. Nonetheless, already in the beginning of the last century chemists realized that some chemical moieties adopt hollow closed-cage structure. Thus, borohydride ions of the form $B_nH_n{}^{2-}$ and carbaboranes, i.e. molecules consisting of boron-carbon and hydrogen atoms, were among the first studied examples of polyhedral structures with an empty core [see Ref. 1]. The stability of these polyhedral structures was attributed to the three atom B-H-B bond, which permits the electron deficient boron atoms to form spatially stable polyhedra with hollow core.

Also early on, it was found that asbestos minerals, like chrysotile (which in its flat form is named lizardite), halloysite, kaolinite, etc. accommodate tubular structures with hollow core. For example, the tendency of kaolinite sheet to fold into tubular structures was studied by Pauling [2]. The stimulus for the curving was attributed to the built-in asymmetry of the layered structure along the c-axis. Each molecular layer of chrysotile (kaolinite) consists of a fused sheet of silica tetrahedra and a sheet of magnesia (alumina) octahedra which are fused together via a common oxygen atom (see **Fig. 1a**). The overall formula of chrysotile is $Mg_3Si_2O_5(OH)_4$ and is $Al_2Si_2O_5(OH)_4$ for kaolinite. The size difference in the (a, b) plan between the two interconnected layers stipulates that the silica tetrahedra occupy the outer face of the scrolling sheet and they are under tensile stress. On the other hand the inner concave alumina octahedra of the asbestos sheet are subdued to compressive stress. This asymmetry leads to folding and scrolling with a clear cut energy minimum as a function of the nanotube (nanoscroll) radius [3]. **Fig. 1b** shows a schematic



(a) (b)

Fig. 1. (a) Schematic side-view (010) of the mineral lizardite (chrysotile in the tubular form); (b) Schematic drawing of a 3-wall chrysotile nanotube (courtesy of Dr. A.N. Enyashin).

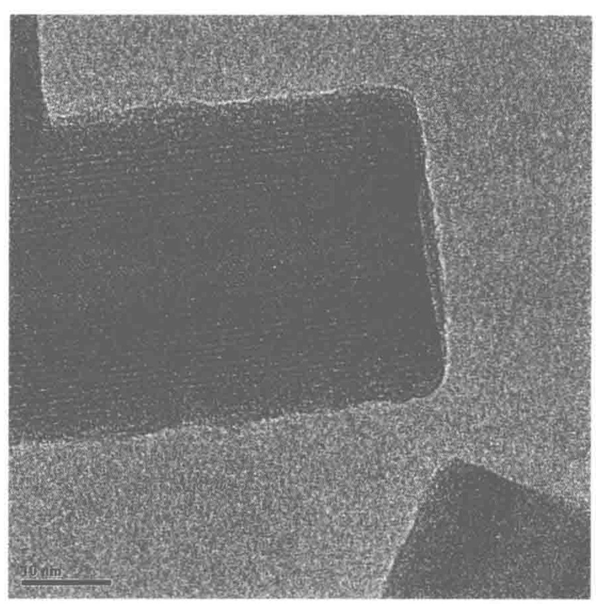


Fig. 2. High-resolution TEM image of the tip of a chrysotile nanotube (courtesy of Prof. N. Roveri and Dr. R. Popovitz-Biro).

rendering of multiwall chrysotile nanotube with clear hollow core in its center, while **Fig. 2** shows a transmission electron microscopy (TEM) of such nanotube. Much attention has been focused on the toxicity of these threaded nanostructures. Interestingly enough though, synthetically produced chrysotile ($Mg_3Si_2O_5(OH)_4$) nanotubes were found to be non-toxic in recent studies [4]. This observation suggests that the asbestos toxicity is rooted in its specific chemical interactions with the human tissues or certain impurities, like iron, and cannot be attributed entirely to its small diameter and large aspect ratio (length to diameter ratio), alone.