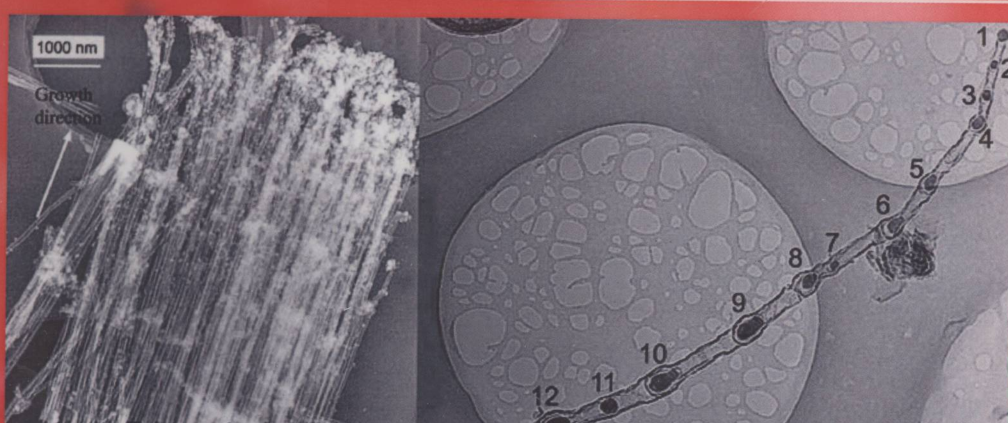
NANOMATERIALS

NEW RESEARCH DEVELOPMENTS



EGOR I. PERTSOV
EDITOR

NOVA

NANOMATERIALS:
NEW RESEARCH DEVELOPMENTS

EGOR I. PERTSOV
EDITOR

Nova Science Publishers, Inc.
New York

For permission to use material from this book please contact us:
Telephone 631-231-7269; Fax 631-231-8175
Web Site: http://www.novapublishers.com

LIBRARY OF CONGRESS CATALOGING-IN-PUBLICATION DATA

Nanomaterials : new research developments / Egor I. Pertsov (editor).
p. cm.
ISBN 978-1-60456-300-9 (hardcover)
1. Nanostructured materials. I. Pertsov, Egor I.
TA418.9.N35N3292 2008
620.1'1--dc22 2007050452

Published by Nova Science Publishers, Inc. ✢ New York

NANOMATERIALS: NEW RESEARCH DEVELOPMENTS

PREFACE

Nanomaterials is the study of how materials behave when their dimensions are reduced to the nanoscale. It can also refer to the materials themselves that are used in nanotechnology. Materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macroscale, enabling unique applications. For instance, opaque substances become transparent (copper); inert materials become catalysts (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon). Materials such as gold, which is chemically inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these unique quantum and surface phenomena that matter exhibits at the nanoscale. This new book presents the latest research from around the globe.

In the last decade, research in nano-materials has revealed a rich variety of phenomena that is affecting a number of fields, such as composite materials, nanoelectronics, sensors, and nanodevices. Among the structural analytical techniques, transmission electron microscopy (TEM), especially high-resolution TEM (HRTEM), has played a key role in the discovery and characterization of novel nano-materials. In the first Expert Commentary, we will report detailed TEM studies on two different types of nano-materials, i.e. fivefold twinned silver nanorods and carbon nitrogen nanotubes.

As explained in the second Expert Commentary, the world of nano-materials burst out quite recently as a novelty in the scientific community, although macromolecules at the nanoscale have been built up by chemists and biologists and quantum effects have been studied by physicists since decades. Nowadays, since the growth of nanomaterial phases and structures can be controlled, applications in nanotechnology related to their chemical and physical properties are almost ready to be achieved. Dendrimers, fullerenes, carbon nanotubes and graphenes, metal and ceramic nanoparticles are all available for the development of advanced technological instruments. Atomic force and scanning probe microscopes, atomic-layer-deposition devices and nanolithography tools can manipulate matter in the atomic or molecular regime. These nanotools are able to control matter at the nano or atomic regime.

The first nanodevice on the market was a quantum dot fluorescent biodetector. MEMS devices are used as accelerometers in automotive airbags. Many other promising applications are pending, such as nanoelectric memory devices, nanosensors, catalysts and drug delivery systems. Components for nanodevices envisage the use of semiconducting organic molecules, polymers and composites.

The first Short Communication is devoted to the investigation of magnetic properties of Pt and Ir nanoparticles. Both Pt and Ir nanoparticles, covered by carbon shell was separated from Pt- or Ir-contained fullerene soot by thermal reaction with acetylacetonate of corresponding metal. Investigation of obtained samplers show that the size of particles influence on their properties: at size decrease the character of electron magnetic resonance spectrum and the magnetization behavior are changed. It is the result of inner state changing of electrons, the most part of which transfer to the localized state with discrete energy levels. This fact is confirmed by the temperature behavior of both magnetization and intensity of electron magnetic resonance lines. Behavior of more large metal particles is like solid metal, but these particles also display magnetic order, which is not a characteristic of solid metal. Such metal particles have super paramagnetic state. Value of the field, at which the magnetization of large particles is saturated, point out increase of magnetic moment per the particle.

Nanostructured temporary scaffolds can be used to surrogate the extracellular matrix and favor the regeneration of tissues and organs. Several techniques have been proposed for scaffolds fabrication, but they all present various limitations. Indeed, it is very difficult to obtain the coexistence of the macro, micro and nano structural characteristics that are necessary for scaffolding application. In particular, several works have pointed out the importance of the scaffold nano-structure to assure a good cellular adhesion and growth. This nano-structure has to mime the part of the extracellular matrix that is composed of collagen fibers. All the previously proposed techniques are unable to obtain this characteristic.

In the second Short Communication a new supercritical fluid assisted technique for the formation of 3D nano-structured scaffolds is proposed; it consists of three sub-processes: formation of a polymeric gel loaded with a solid porogen, drying of the gel using SC-CO_2, washing with water to eliminate the porogen. The authors obtained 3D Poly(l-lactic acid) scaffolds with elevated porosity (> 90%) and a good interconnectivity, characterized by both a fibrous nanostructure with fibres ranging between 50 and 500 nm and micronic cells, adequate mechanical properties (up to 81 KPa) and very low solvent residue (< 5 ppm). It is possible to control both the nanostructure morphology and size modifying the gelation procedure and/or changing the polymer concentration and the connection between the micro and the nanostructure changing the porogen dimension and quantity and/or the loading procedure.

Based on the authors' experience of conventional crystal growth of $A^{II}B^{VI}$, we have developed the techniques for nanocrystal production of some of these compounds.

Further innovations in the technological process appear to significantly reduce the development and production cost of the final product with respect to conventional single crystals, while maintaining a high level of physical properties, which conform to leading standards.

New technology of the vapor phase deposition was developed in the authors' laboratory to produce CdTe nanoparticles of average diameter 8 nm. Further development of the technology allows them to produce 10-nm Cd-Zn-Te nanocrystals and to overcome difficulties in obtaining a ternary solid solution $Cd_{1-x}Zn_xTe$ ($x = 0.04$—0.1) with a stable chemical composition. Highly dense CdTe and $Cd_{1-x}Zn_xTe$ ceramics of high mechanical hardness and durability were produced by the room temperature process without any lubricants or binding materials.

It was found that CdTe ceramics produced from nanocrystals undergo wurtzite—sphalerite transition under pressure. The polymorphic transition from the hexagonal to the cubic phase in $Cd_{1-x}Zn_xTe$ ceramics caused by annealing is discussed in the third Short Communication.

The two-component texture composed of <220> axial and {100}<hk0> components was recorded in the as-compressed materials.

The effect of annealing on grain growth and texture in the ceramics is considered. It was found that our compacted ceramics guarantees high transmittance in a wide IR region of 6—25 μm, high specific resistivity on the order of 10^{10} Ωcm, and high microhardness on the order of 10^3 MPa.

The obtained properties make these materials promising for use in IR optics and for ionizing-radiation detectors.

As presented in Chapter 1, one-dimensional structured (1D) nanofiber materials have attracted great interest over the past decade because they can potentially address many advanced applications involving dimensionality and size-confined quantum phenomena. Compared with non-dimensional nanoparticles, the 1D structure of nanofiber materials lend them the anisotropic properties suitable for fabrication of nanodevices. They are expected to play a crucial role as interconnects and functional units in fabrication of lab-in-chip, electronics, electronichemical, optoelectronic and electromechanical devices with a nanoscale dimension. In addition, nanofiber materials have been found to have broad application potentials in various other areas, such as advanced ceramics, metal/composite reinforcement, membrane separation, sensor, catalysis, biological and biomedical fields.

1D nanomaterials with different aspect ratios and morphologies can be generally classified as nanorods, nanowires, and nanotubes. Nanorods are usually straight 1D nanostructured materials with a diameter of 1~100 nm and low aspect ratios of 3 – 20. Nanowires are wire-like nanomaterials with larger aspect ratios than nanorods and usually nanowires exhibit curly morphology, although there is not a clear criterion to distinguish nanorods and nanowires. Some nanowire materials have ribbon-like, belt-like or whisker-like morphology, and they are called nanoribbons, nanobelts, and nanowhiskers with a more precise definition. Nanotubes are a kind of 1D nanofiber material with hollow-structures, although the length and aspect ratio vary.

Many synthesis methods have been developed for generating nanofiber materials with various structures. Among these methods, vapor-liquid-solid (VLS) process, vapor-solid (VS) reaction, laser ablation, solution-liquid-solid (SLS), hydrothermal/solvo-thermal sol-gel and electrospining routes have been extensively explored. Other techniques make use of a straight nanochannel structure, such as SBA-15 and porous anodic aluminum oxide (AAO), as hard template, or deploy liquid crystal and surfactant as soft template. The recent advances in synthesis and development of nanofiber materials and the potential applications of these 1D nanostructured materials are summarized in this chapter. Potential hazard associated with the research and practical application of nanofiber materials are also addressed. The corresponding materials are organized into three main sections: (1) Preparation methods, (2) applications of nanofibers and (3) risk assessment of nanofiber materials toward application.

Evolvement of bioinspired techniques for the construction of well-ordered nanomaterials is a crucial intersection of branches of materials science and biotechnology. Soft chemistry technique is presently developed to fabricate a variety of functional nanostructures through appropriate biogenic approaches.

In Chapter 2, a series of inorganic nanostructures with various morphology and size, have been successfully prepared and encrusted on degummed silk fibroin fibers (SFF) or eggshell membrane fibers (ESMF), respectively, through in situ biotemplate soakage approaches at room temperature. Some amino acids of the SFF or ESMF mainly provide both the reactants and location functions under different solution conditions. The pattern and the hierarchy of as-prepared hybrid nanocomposites, containing inorganic nanocrystallites on some biofibers, mostly depend on the composition and the status of the impregnant solutions as well as the particular configurations and the special functional groups of SFF and ESMF biomacromolecules. Herein, the biofibers not only serve as the substrates, their biomacromolecules but also function as the templates and the surfactants, thus small-sized, well-distributed, and well-crystallized inorganic nanoparticles can be organized into subtly hierarchical nanoarchitectures combining organic biofibers to form well-organized inorganic-organic hybrid nanocomposites.

The as-formed inorganic nanocrystallites not only have good quantum size effect and dispersancy, but also exhibit excellent biocompatibility when combined with the biofibers SFF or ESMF, which would make the hybrid nanocomposites promising for the applications in photoelectric, photonics, photocatalyst and photoelectron transfer devices. This bioinspired technique also provides a sort of green, moderate and effective strategy for the synthesis of other series of functional nanomaterials with pre-desired conformation and relevant valuable properties.

Morphological control of TiO_2 nanocrystals with high crystallinity is a big challenge. Recent progress of synthesis and application of titania nanomaterials, especially application for dye-sensitized solar cells, were overviewed. Chapter 3 reviews the formation procedures and characterization of titanium dioxide nanocrystalline products, which exhibit various morphological shapes in nanometer scale, i.e., nanotubes, nanorods, nanowires and nanosheets, and some of their arrays. There are three main research trends in fabrication of nanoscale titania materials and their applications. (1) Hydrothermal synthesis method of nanoscale titania or titanate in aqueous alkaline solutions. Highly crystallized nanoscale titania with various morphology were synthesized based on the studies on mechanistic understanding. (2) Highly ordered nanotube arrays of titania by anodic oxidation of titanium metal. Detail reaction conditions have been studied to provide better quality nanotubes for various applications. (3) Molecular titanate nanosheets have been synthesized and invite a range of applications by providing a well-ordered monolayer and multilayer thin films from titanate nanosheets with electronic, catalytic, and other properties. These recent three research trends are fully overviewed, together with other titania nanoscale materials, such as, nanorods, nanowires. We also present new findings in our laboratory on the formation of titania nanorods and network structure of single-crystal-like titania nanowires as well as their application for dye-sensitized solar cells.

Nowadays, chemical sensors find application in many technological fields, such as environmental, industry, medicine, automotive, etc. Due to their simple structure and low cost, Metal Oxide Semiconductor (MOS) resistive sensors represent the more investigated typology. In order to enhance their performance, the synthesis of various nanosized metal oxides has provided new impulse. Nanostructured materials are of interest both for basic scientific research and technological applications as their properties depend on their extremely large specific surface areas. Furthermore, their surfaces have generally unique properties which greatly differ from those of bulk materials. Because of the high surface-tovolume ratio, local phenomena such as adsorption or modification of the electronic structure at the surface may contribute significantly to the sensing properties of the materials. In Chapter 4 the authors review the synthesis and characterization of representative metal oxides nanoparticles by non-aqueous sol-gel approaches. These techniques allow the preparation of nearly monodisperse and highly crystalline nanoparticles. Their sensing properties and possible utilization in technologically relevant devices are thoroughly presented.

The conjugation of enzymes to nanoparticles is of great importance in Bionanotechnology and Nanomedicine. The question is how to proceed without affecting the catalytic activity of the enzyme. This constitutes a difficult task since any small variation in the conformation of the enzyme affects its catalytic activity. Enzymes conjugated to nanoparticles have been used mainly as redox mediators in biosensors and as smart nanodevices for targeting specific cells and tissues. Chapter 5 is only centered on this latter issue. Enzymes can be conjugated to nanoparticles through: a) covalent association of the enzyme to the surface; b) entrapment of the enzyme in a polymeric matrix adsorbed on the surface, c) supramolecular association with molecular receptors capping the surface, which is the method developed by the authors, based on the association of enzymes to nanoparticles capped with perthiolated cyclodextrins.

Wild enzymes, or previously modified with adamantane moieties, have been used and the best results were obtained with modified enzymes. The supramolecular procedure assists the retention of the conformation of the enzyme. Even more, in some cases the formation of a more compact conformation has been observed, especially when using perthiolated gamma-cyclodextrin as the capping agent. A bienzymatic anti-oxidant nanoparticle system containing copper(II)-zinc(II) superoxide dismutase and catalase has been obtained using this procedure. A similar procedure has been used to prepare new biosensors.

In recent years, the scientific interest towards the chemistry of noble metal nanoparticles (NPs) has been growing exponentially. In particular, Au-NPs have been the subject of several thousand studies, dealing with synthesis, characterization, or application issues. Tents of different routes have been proposed for the controlled preparation of colloidal gold nanostructures. Chapter 6 illustrates how electrochemistry can be proficiently applied to the size- and shape-controlled synthesis of gold nano-colloids. Compared to other bottom-up nanofabrication procedures, the electrochemical synthesis of metal NPs offers advantages such as the absence of reducing chemicals and the possibility to tightly control the NPs morphology by means of simple process parameters. The whole synthetic procedure is quite easy to perform, and compatible with scaling-up perspectives. However, critical is the choice of the experimental conditions, such as the working potential, the current density, and the electrolyte composition. A proper combination of electrochemical parameters and chemicals' reactivity opens the way to different morphologies. NP size and shape can be separately tuned, thus leading to spheres, rods, wires, cubes, triangular plates, dumbbells with different properties. The spectroscopic characterization of electrosynthesized NPs shows interesting size-dependent features that can be used for diagnostic purposes both in surface- and bulk-analysis contexts. Unpublished results from the authors' lab are reported as well.

New nanomaterials can be used in a number of forthcoming buildings-related technologies in order to accomplish benign indoor environments. Chapter 7 takes a unified view on such technologies from a solar-energy-related perspective. Specifically, electrochromics is discussed as a technology to give user-adapted daylighting and avoid glare and thermal discomfort due to excessive solar influx. Solar photocatalysis is introduced with regard to air purification, and the demand for ventilation is monitored via sensors for air quality. Nanocrystalline and nanoporous transition metal oxides are employed for all of the various functions, which clearly shows that the research field outlined in this brief review has a high degree of internal consistency and even, in many cases, makes good use of the same type of materials for different applications. The presentation is focused on recent results from the authors' laboratories.

Chapter 8 studies bone cements incorporated with montmorillonite (MMT), which were prepared in an attempt to improve their mechanical properties. The cements were characterized using particle size analysis, gel permeation chromatography, viscosity measurements, unreacted monomer analysis, X-ray diffraction, transmission electron microscopy, energy-dispersive X-ray spectroscopy, and mechanical properties. The average particle size and molecular weight of the PMMA powders used were 47μm and 100,000g/mol, respectively. The incorporation of MMT led to an increase in viscosity of the bone cement but did not severely affect its setting temperature or the amount of residual monomer. Regardless of the MMT mixing methods used, in this case MMT being mixed with liquid and powder components, sodium MMT (SMMT) was not well dispersed in the bone cements, which was believed to be due to its hydrophilicity. Organophilic MMT (OMMT) was better dispersed in the liquid component than in the powder component. The compressive and tensile strength of the bone cement containing the OMMT mixed into the liquid component were significantly higher than those of the bone cement without MMT ($p<0.05$).

CONTENTS

EXPERT COMMENTARIES

In: Nanomaterials: New Research Developments
Editor: Egor I. Pertsov, pp. 3-11
ISBN: 978-1-60456-300-9

STRUCTURAL CHARACTERIZATIONS OF NANO-MATERIALS BY TRANSMISSION ELECTRON MICROSCOPY

R.C. Che, H.Y. Chen and J.Q. Li[1]
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, China

1. INTRODUCTION

In the last decade, research in nano-materials has revealed a rich variety of phenomena that is affecting a number of fields, such as composite materials, nanoelectronics, sensors, and nanodevices. Among the structural analytical techniques, transmission electron microscopy (TEM), especially high-resolution TEM (HRTEM), has played a key role in the discovery and characterization of novel nano-materials. In this chapter, we will report detailed TEM studies on two different types of nano-materials, i.e. fivefold twinned silver nanorods and carbon nitrogen nanotubes.

Firstly, remarkable fivefold twinning structure with five {111} twinned subcrystals has been observed from the cross-sectional Ag nanorods. Careful examinations revealed that the Ag nanorods in general have a pentagonal shape with fivefold axes going along the [110] zone axis. The twinning relationships and local structural distortions on all five twinning boundaries have been carefully examined by HRTEM observations and FFT processing. Additionally, we have carried out an extensive TEM study of the microstructural properties of carbon nitrogen nanotubes with encapsulated Fe_2O_3 particles. The local structural and chemical features were examined by using nano-electron diffraction and electron energy loss spectroscopy (EELS). The experimental results demonstrate that the number and spacing of the encapsulated Fe_2O_3 particles inside a nanotube can be controlled very well by adjusting the synthesis parameters. The doped nitrogen atoms in carbon nanotubes give rise to a visible

[1] E-mail address: LJQ@aphy.iphy.ac.cn Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China, Corresponding author.

π^*-type peak at around 399 eV in the experimental EELS spectra. These results might shed light aiding the understanding of the structure of such novel structures at an atomic scale.

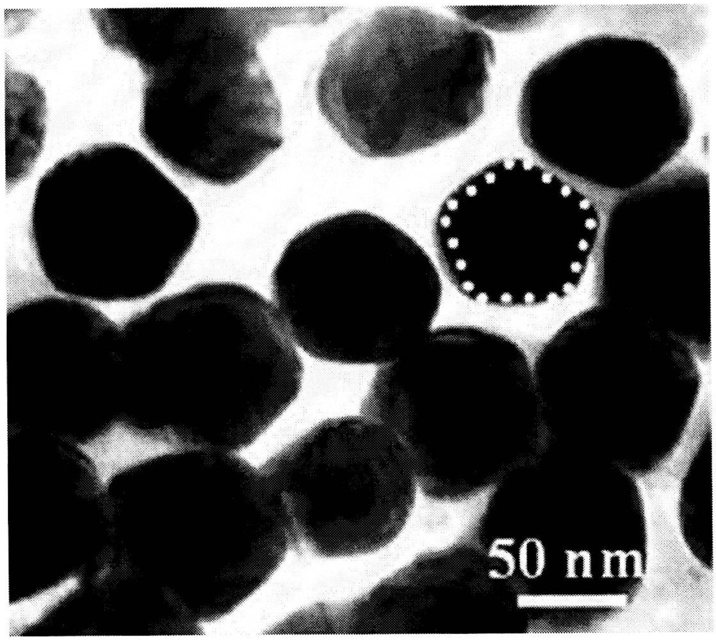


Figure 1. TEM image showing the pentagonal profile of the nanorods.

2. Transmission Electron Microscopy Study of Fivefold Twinned Silver Nanorods

A good understanding of the microstructural properties is obviously the key point for obtaining nanoparticles and nanorods (nanowires) with desired properties. Ino[1] first proposed a multiple twinned particle (MTP) model in small clusters for understanding decahedral and icosahedral structures. Marks *et al.*[2,3] reported icosahedral multiple twinned nanoparticles consisting of 20 tetrahedra twinned on their {111} planes. Recently, nanorods (nanowires) with some specific sizes, shapes, and symmetric properties have been studied. For instance, copper nanorods were prepared by the polyol process, such Cu nanorods are held to be truncated decahedra with fivefold symmetry.[4] Hofmeister[5] reported certain microstructural properties of multiple twinned silver nanoparticles with a rod-like shape. Well defined silver nanorods (nanowires) are desirable for their optical and electronic properties. Methods for preparing Ag nanorods have been reported in the literature[6-11]. There have been a few TEM studies of Ag nanorods, with most focusing on determining the fundamental structural features. Recent studies[12-13] suggest that this kind of metal nanorod shows a fivefold twining structure; however, no direct experimental evidence on the cross-sectional structure was reported to characterize this remarkable twinning nature. Here, we systematically investigated the fivefold twinning structure in silver nanorods by TEM.

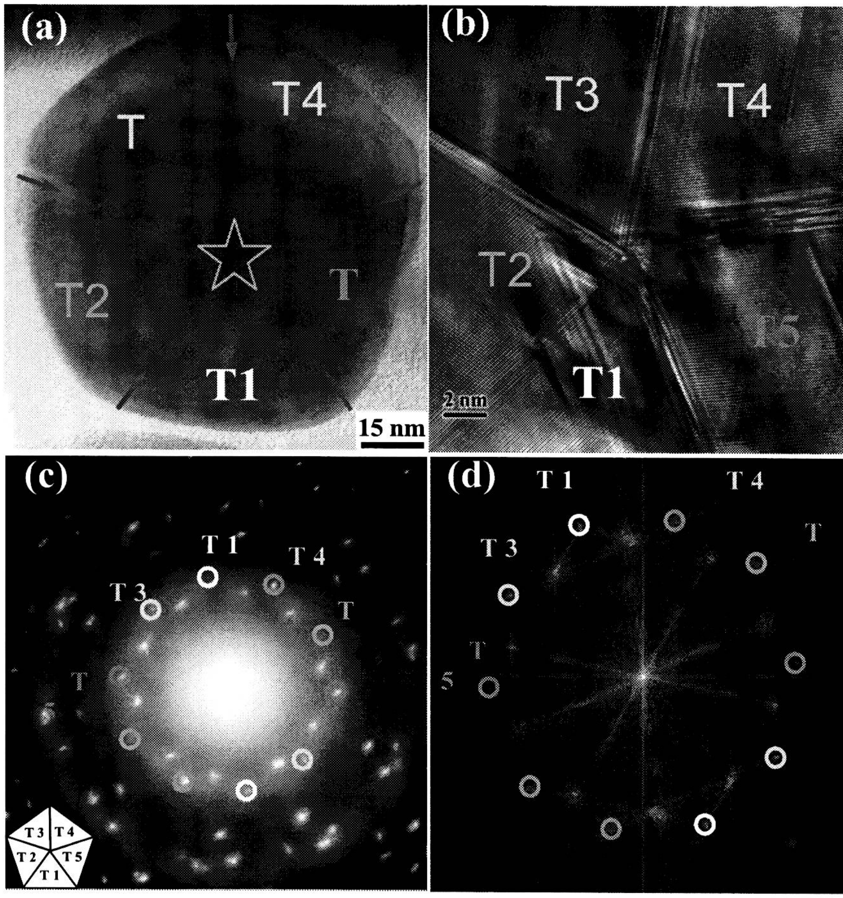


Figure 2. (a)Low-magnification and (b)high-magnification cross-sectional TEM images of the five juxtaposed crystals. (c) Electron diffraction pattern and (d) FFT image of Figure 2(b).

A. Cross-Sectional Structures of Ag Nanorods

Detail process for preparing pentagonal Ag nanorods has been described in Ref. [14]. Figure 1 shows a typical transmission electron microscopy (TEM) micrograph illustrating the presence of Ag nanorods. The diameter ranges from 20 to 100 nm. The profiles of Ag nanorods appear as clear pentagonal sections as denoted by the dashed lines.

Figure 2a shows a low magnification TEM image indicating clear boundaries of a pentagonal Ag slice (marked by arrows). The different contrasts inside the twinning boundaries are due to the presence of microtwins and stacking faults in the silver matrix. Figure 2b shows the HRTEM image, in which the lattice fringes within Ag subcrystals and near their boundaries can be clearly recognized.

The TEM images in Figure 2a and 2b show the presence of five distinctive boundaries in the cross-sections of Ag nanorods; the five subcrystals are labeled as T1, T2, T3, T4, and T5, respectively. To get the HRTEM micrographs to reveal the atomic structural features of the pentagonal sections, we invested a lot of effort to find the specific slices of the pentagonal