

Chapter 1

Introduction

In the past decades, nanoscience and nanotechnology has been making significant progress, and the effect of nanoscience and nanotechnology on every field has been acknowledged in the world. Therefore, in the 21st century, their strategic position has already been established. The study of nanomaterials and nanostructures is one field with the earliest starting that obtained rich achievements in nanoscience and nanotechnology. Nanomaterials and nanostructures play a very important supporting role for applications of nanoscience and nanotechnology in the field of fabrication, such as information and techniques, energy sources, environments, health and medical treatments. All countries place the study of nanomaterials and nanostructures in a very important position. While the United States arranges the development of the front fields of nanoscience and nanotechnology, such as nanoelectronic technologies and devices, nano- and micro-fabrication techniques, nanobiotechnology, nanomedicines and diagnosis techniques, nanoenvironmental monitoring and treatment techniques, the continuation of the in depth study of nanomaterials and nanostructures is placed in an extremely important position. In the investment for the study of nanoscience and nanotechnology, the investment for nanomaterials and nanostructures occupies 49%. This sufficiently indicates the guiding role and the importance of the study of nanomaterials and nanostructures. Now, the motivational power of the study of nanomaterials and nanostructures are mainly national strategy requirements and enhancements of the national competitive ability in the high science and technology field. In addition, the in depth study of nanomaterials and nanostructures is an important source for producing new principles, new techniques and new methods, and potentially leading to breakthroughs in great scientific problems. At the same time, the nanomaterial market is also a native power for the development of nanomaterials. It will stimulate and promote the development of nanomaterial and nanostructures.

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The high technique field requiring nanomaterials with unique properties is the important motivational power for drawing the nanomaterial development to new depths. In the IT industry, the fabrication of ultramicrochips will inevitably drive the sizes of CUP, transistors, high-density storage, field emission displays, ultraspeed calculation and logical devices towards the nanometer sizes. This makes the requirement of nanomaterials with unique properties more urgent. When the line width made by lithography becomes the order of nanomaterials and the CMOS circuits decrease to the ultramicro sizes, the requirement of nanomaterials and nanostructures with stable properties becomes more urgent. Fabricating the nano-sized optoelectronic devices is likely to push the IT industry development to a new level. The study of nanomaterials and nanostructures will be faced with a strict challenge as a result.

The high sensitivity, high resolution nanofluid biodetectors, virus and bacterium detection and diagnosis, cell restoration, rapid diagnosis of the diseased position, carriers of target treatment, early rapid detection of toxic gases and burnable gases, rapid diagnosis of explosive molecules, etc., fields are developing at a high speed. This will make nanomaterials and nanostructures become inevitably one of the mainstream materials, and this also proposes a new challenge for the study of the unique properties of nanomaterials and nanostructures.

The rapid progress of global industries and the promotional requirements of traditional industries will encourage nanomaterials and nanostructures to play an important role in our competition. This will inevitably raise the fabricating technique and applied technique of nanomaterials and the study of optimization of structures and properties of nanomaterials to a new level.

Nanomaterials and nanostructures are established as the knowledge frame of an important branch of learning. This will promote the study of nanomaterials and nanostructures to develop deeply and expansively. Although the preparation science of nanomaterials made remarkable progress, such as the synthesis of a series of materials with new structures and new properties which has never been seen in the traditional material field, and the discovery of some special physical properties and proposal of some new concepts, the field of nanomaterial as a new branch of learning did not develop perfectly. A description of the new and unique physical and chemical phenomena which were discovered, still stops at the explanation step when using the traditional theory. In a strict sense, the relatively independent new theory of nanomaterials and nanostructures has

yet to be established. The research of new laws is not systematical. The new effects appeared in the nanofield, such as the quantum confinement effect and coulomb blockade effect etc., are also established according to the traditional quantum theory. Different from the thermodynamics of infinite systems, for establishment of the thermodynamics of nanomaterials systems, controlled growth dynamics of nanomaterials, new laws of matter and energy transport of nanosystems, new principles and new methods of regulation and control of structures and properties etc., all have expansive knowledge innovation spaces. The research of nanomaterials and nanostructures at the new step is expanded around the above-mentioned scientific problems. It will inevitably provide the basis for designing nanomaterials with special structural control of the properties of nanomaterials and nanostructures. Therefore, an establishment of the self-scientific frame of nanomaterials is a significant and extremely difficult assignment. It must be established on the basis for a deeper study of nanomaterials and nanostructures. Now, our important assignment is to realize "three transitions" based on the nanomaterial research, and push nanomaterials to develop towards a newer more profound level. One is that the preparation realizes scientifically the transition from random growth to controlled growth, and the growth dynamics of nanomaterials, nanostructures and the thermodynamics of the confinement systems are studied. The second one is the transition from the exploration of random new phenomena to the more profound exploration of new laws. The conditions for unique property appearance, the change laws of properties and the factors which affect the property stability are systematically studied, so that the properties become controllable. The third transition is that of the research focus of gravity from preparation and synthesis as the main focus to the study of the relation between nanomaterials and nanostructures. The study of the law and process of nanostructure development and the effect on properties, and the investigation of the relation of preparation processes, nanostructures and properties, theoretically provide the theoretical basis for designing nanostructures with the required properties and obtaining the required properties and structures through the preparation methods. When the sample size reaches the order of nanometers, this does not imply the appearance of new properties. The new properties occurring in single element nanomaterials and nanostructures certainly do not satisfy the applied requirements. Therefore, through heterogeneous doping, composite and heterogeneous nanostructure designing, the largest limit excavation of nano effects and optimization, modulation and control of properties are realized. All of these problems are the most challenging problems in the research field of nanomaterials and nanostructures, and are also the important market of the deep research of nanomaterials and nanostructures.

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In the past decades, significant progress has already been made in the field of zero- (0D) and two-dimensional nanomaterials and nanostructures, since the discovery of pure carbon nanotubes,¹ and one-dimensional (1D) nanomaterials have stimulated great interest. Due to their potential interests to the understanding of physical concepts and for applications in constructing nanoscale electronic and optoelectronic devices,^{2–8} they are the ideal systems for investigating the dependence of electrical transport, optical and mechanical properties on size and dimensionally and are expected to play important roles as both interconnects and functional components in the fabrication of nanoscale electronic and optoelectronic devices.⁹ Up to now, 1D nanomaterials and nanostructures, such as nanotubes,^{10–12} nanorods,^{13–15} nanowires,^{16–18} nanobelts or nanoribbons,^{19–21} nanocables,^{22–25} and nanosheets,^{26–28} have been successfully synthesized by a variety of methods.

During the past decade, many methods have been developed to synthesize 1D nanomaterials and nanostructures. Overall, they can be categorized into two major approaches based on the reaction media that were used during the preparation: solution and gas phase-based process. Solution-based approaches include template-directed synthesis,^{29–33} solution-liquid-solid method,³⁴ and solvothermal chemical synthesis.^{35–38} Gas phase-based process for 1D nanomaterials and nanostructures mainly include four growth mechanisms. One is a well-accepted so-called vapor-liquid-solid (VLS) process of nanowire and nanowhisker growth proposed by Wagner and Ellis.³⁹ According to this mechanism, the anisotropic crystal growth is promoted by the presence of the liquid alloy/solid interface, and the detailed description about the VLS growth mechanism can be found in the literature by Yang.⁴⁰ It is conceivable that the size and diameter of the as-synthesized products can be controlled by selecting different size catalysts. For example, monodisperse silicon nanowires were synthesized by exploiting well-defined gold nanoclusters as catalysts for 1D growth via a VLS mechanism in the Lieber group.⁴¹ Transmission electron microscopy (TEM) studies of the materials grown from 5, 10, 20, and 30 nm nanocluster catalysts showed that the nanowires had mean diameters of 6, 12, 20, and 31 nm, respectively, and were thus well-defined by the nanocluster sizes. The positions of 1D nanostructures can be controlled by the initial position of Au or other catalyst clusters or thin films. In addition, by applying the conventional epitaxial crystal growth technique into the VLS process, it is possible to achieve precise orientation control during the nanowire growth. Second is the vapor-solid (vs) growth process. In this process, vapor is first generated by evaporation, chemical reduction or gaseous reaction. The vapor is subsequently transported by a

carrying gas, and condensed onto a substrate. Some metal, oxide and other nanomaterials and nanostructures have been successfully synthesized by the VS process.^{29,42–44} It is generally believed that growth temperature and gas-phase supersaturation determine the growth rate of surface planes and the final morphology of the crystals, with other experimental parameters playing minor roles in the VS process. Third is oxide-assisted growth, which is a new nanowire growth route proposed by Lee⁴⁵ This synthesis technique, in which oxides instead of metals play an important role in the nucleation and growth of nanowires, is capable of producing a series of nanowires. Fourth is the combination of the anodic alumina membrane (AAM) and chemical vapor deposition (CVD). For example, Zhang reported that large-scale single crystalline GaN nanowires in anodic alumina membrane were achieved through a gas reaction of Ga₂O vapor with a constant flowing ammonia atmosphere at 1273 K.⁴⁶ Ordered ZnO nanowire arrays have also been fabricated via this method by Lee⁴⁷

Exploration of nanomaterials and nanostructures that exhibit functionality is the key to nanotechnology. Among the 1D nanomaterials and nanostructures, functional oxides are the fundamental ingredients of smart systems, because the physical and chemical properties of the oxides can be tuned and controlled through adjusting cation valence state and anion deficiency. The structures of functional oxides are very diverse and colorful, and there are endless new phenomena and applications. Such unique characteristics have made oxides the most diverse class of materials, with properties covering almost all aspects of condensed matter physics and solid state chemistry in areas including semiconductivity, superconductivity, ferroelectricity, magnetism, and piezoelectricity.⁴⁸ Up to now, much attention has been paid to the preparation of binary oxide nanomaterials and nanostructures.⁴⁹

An important issue in the self-organized growth and application of 1D nanomaterials and nanostructures is how to control the composition, size, morphology, position, orientation and crystallinity etc. in an effective and controllable way. The significance of the controllability manifests in both the chemistry of small-size material synthesis and the realization of their applications. A significant challenge for the chemical synthesis is how to rationally control the nanostructure assembly so that their size, dimensionality, interfaces, and ultimately, their two-dimensional and three-dimensional superstructures can be tailor-made towards desired functionality.⁴⁰ Controllable synthesis of nanowires and nanobelts only started to emerge recently.

8 Bibliography

This book will introduce the new methods and principles about the controlled growth of a nanomaterial system in detail, including a simple nanomaterial system, an ordered nanostructure system and a complicated nanostructure ordered system, the essential conditions for the controlled growth of nanostructures with different morphologies, size, compositions, and microstructures, and we also discuss the dynamics of controlled growth and thermodynamic characteristic of the two-dimensional nanorestricted system. This book also introduces some novel synthesis methods for nanomaterials and nanostructures, such as hierarchical growth and some developing template synthesis methods etc. combined with the application of nanomaterials and nanostructures. This book introduces correlative novel properties and property control arising from nanomaterials and nanostructures. This book also reviews the developing trend of nanomaterials and nanostructures.

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