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The New Frontiers of Organic and Composite Nanotechnology

Editors

**Victor Erokhin, Manoj Kumar Ram
and Ozlem Yavuz**

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Preface

Currently, the term nanotechnology is used to refer to the realized structures whose characteristic sizes are less than 100 nm. Nanotechnology has found special applications in most fields of modern science and technology. Realization of objects with decreased dimensionality (up to zero-dimensional quantum dots) provides new possibilities for fundamental researches connected to quantum phenomena, which cannot be observed on bulk materials. The applied aspects of nanotechnology are also very important. The method of modification of material surfaces with molecular layers has diverse applications such as corrosion inhibition, anti-friction, smart surface realization, etc. In electronics and communication systems, nanotechnology offers to increase the speed of information processing and integration. With respect to biomedical applications, new effective and reliable sensoristic systems have been developed based on the utilization of specific bioorganic molecular layers and conjugates of biomolecules with polymers and/or nanoparticles. Presently, new smart systems for directed drug release are under development.

The aim of this book is to review the current status and future perspectives of researches in different branches of nanotechnology, with the key focus on organic and composite systems. Organic materials attract increasing attention due to their unique properties, which allow the realization of a wide variety of working systems. Many of these properties, especially those connected to the functioning of biological molecules, cannot be reproduced with inorganic materials. In addition, organic materials are lightweight and have high flexibility. However, one serious drawback in them is decreased stability with respect to inorganic materials. Therefore, the current activities in this field are directed to the search of new compounds (mainly polymers), which are expected to significantly improve the stability, allowing, therefore, to widen the applications of organic materials. In parallel, organic-inorganic composites can produce hybrid structures, which combine the sound features of both types of compounds.

Each chapter of this book is connected to a unique aspect of nanotechnology. We begin with the description of layer-by-layer self-assembling,

which currently finds a lot of applications due to its simple realization process and the potential to develop a wide variety of functional molecular systems. Nanoengineered polymeric capsules have attracted a lot of attention immediately after it was first reported in 1998. These objects are very popular among researchers for several reasons. From a fundamental point of view, these systems allow to study growth processes and properties of space-confined matter. One of the most interesting properties of capsules is the possibility to open and close reversible pores in their shells. In particular, this property can be very useful for the development of smart drug-release systems. In the subsequent chapter, we describe the current status of applications of advanced optical spectroscopies to nanotechnology, including single-molecule spectroscopy and the latest achievements in the possibility of signal-pronounced enhancement. A separate chapter is dedicated to give an overview of compositions and properties of hybrid conducting materials formed from different guest molecules incorporated into the host matrix. One important feature of organic and composite materials is the possibility to vary their properties by redox reactions. Two chapters are dedicated to the utilization of these properties. One chapter demonstrates how it can be used in scanning probe microscopy, while the other describes the electrochemical elements that can be used for adaptive network realization. Two successive chapters deal with the biomedical applications of nanotechnology. In particular, the present developments of enzymatic and immunosensors are reviewed. Finally, electromagnetic applications are considered.

To my belief, each chapter of this book offers a critical approach to the description of the available techniques and investigation methods to provide a better understanding of their strong and weak points as well as their limits and areas of applications.

Victor Erokhin

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Chapter 1

Layer-by-layer assembly

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Abstract. Layer-by-layer self-assembly has several merits including low process temperature, molecular resolution of composition, thickness control and a wide variety of appropriate building blocks. From the time it was first demonstrated, it has been widely used by researchers in different disciplines. The alternate adsorption of oppositely charged macromolecules is able to produce complex heterogeneous architectures for optical devices, synthetic catalysts and especially man-made biological components. The principle, operation and characterization of this unique technique are discussed in the first part of this chapter. In the later part, the fabrication conditions and the current and future applications are addressed.

Keywords: layer-by-layer self-assembly, electrostatic interaction, nanostructured materials, nanocomposites, macromolecules

1.1. Introduction

It is always exciting to observe the miracles in living organisms through their unceasing, precise self-assembly of proteins, DNA and bones. In spite of its complexity, self-assembly is commonly recognized as one of the ultimate goals of nanoscience and nanotechnology. In the recent past, the semiconductor-based microfabricating technology helped people to produce structures at a length scale that has never been achieved before. Thin films could be made via molecular beam epitaxy, spin coating, thermal evaporation, sputtering and chemical vapor deposition. Micron-meter scale patterns can be reliably generated. However, with the constant reduction of

the feature size, self-assembly gradually reveals itself one of the ultimate means to manipulate the building blocks in a much smaller world.

So far, the existing self-assembly approaches are classified according to different processes and inter-molecular interactions. The Langmuir–Blodgett (LB) approach was mainly based on van der Waals interactions [1]. It allows to deposit multilayers by transferring a set of monolayers preformed on water surface onto solid substrate surfaces. Another approach, namely the self-assembled monolayer (SAM), was based on the attachment of thiol monolayers to the gold surface, which is due to strong bonds between the sulfur atoms of the thiol group and gold surface [1]. Even if both the above mentioned methods can control the molecular order in the film, they are limited by the thickness of the film, availability of building blocks, and substrates and versatility of the process. Layer-by-layer (LbL) self-assembly is an alternative approach to overcome the above drawbacks. It makes use of alternate adsorption of oppositely charged macromolecules resulting in the self-organization of films and new composites. It controls the precise order of deposition of molecular layers as well as thickness up to 1~2 nm resolution. It significantly broadens the availability of building blocks and substrates because all charged macromolecules can be assembled onto the surfaces of charged substrates. The advantages enable the engineering of the macroscopic electrical, optical, magnetic, thermal and mechanical properties of the composites, which is important for many engineering devices and applications. There is no difficulty in constructing a c. 500 nm thick multilayer with a predesigned sequence of depositing different molecules. Its capability to self-organize a large number of biological substances such as proteins, including enzymes, and DNA allows a wide range of applications in the area of nanobiology. The regular dipping motion of the LbL assembly can be readily converted into the automatic manner for mass production.

The first report on electrostatically driven LbL self-assembly of inorganic colloidal particles can be traced to the work of Iler [2]. Iler showed that oppositely charged silica and alumina particles could be electrostatically self-assembled in multilayer structures by alternate successive immersing of the substrate into two colloidal solutions. In 1990s, Decher et al. had demonstrated the LbL self-assembly of cationic and anionic polyelectrolytes. Subsequently, they showed the possibility of the formation of similar multilayer structures consisting of combinations of charged colloidal particles and biomacromolecules such as DNA [3–5]. Soon, the method became very popular as different research groups had used this technique to realize assemblies containing charged polymers [4–8], proteins [6,7], nanoparticles [9–11], dyes [12–14] and clay nanoplates [15–17].

1.2. Layer-by-layer Self-assembly

1.2.1. Basic Principles

The alternate adsorption of molecular monolayers is mainly based on electrostatic interactions between the neighboring layers. Therefore, it is often referred to as electrostatic self-assembly (ESA). When the polyanion, such as poly(styrenesulfonate), is dissolved in water, the sodium cations are dissociated from the molecule backbone at appropriate pH that is away from the isoelectric point, leaving the long molecule chain negatively charged (Fig. 1.2). For the same reason, the ionized polycation chain is positively charged. Of course, the entire solution appears electrically neutral. The LbL self-assembly involves the alternate successive dipping of a solid substrate into solutions containing anionic and cationic molecules. When the polycationic molecules approach a negatively charged substrate within a sufficiently small distance (Debye length), the local electric field is so strong that it attracts molecules to the surface. The diffusion mechanism in the solution constantly provides the availability of molecules near the substrate surface. The surface is, therefore, completely covered by a layer of cationic molecules that compensate the charge of the previous layer and make the substrate surface positive with respect to the solution. The surface electrical polarity is completely reversed, and the sample can then be used as a template to attract negatively charged molecules during subsequent dipping.

The procedure of LbL self-assembly is illustrated in Fig. 1.1. In Fig. 1.1a, the negatively charged substrate is immersed into the polycation solution. The polycations are adsorbed on the substrate surface within an optimized duration depending on the type of molecules. Later, the substrate is taken out of the solution, rinsed in deionized water (DI water) for several minutes and then dried by a nitrogen jet. Subsequently, the substrate is immersed in a polyanion solution, rinsed and dried in the same way as above. Alternate dipping enables the formation of predefined polycation/polyanion multilayers. Fig. 1.1b illustrates the application of LbL self-assembly for the formation of composite films consisting not only polyions but also proteins, dyes and nanoparticles in a designed sequence.

Rinsing is quite important as it removes weakly attached, physically adsorbed components, thus preparing the surface for subsequent adsorption [18]. It also guarantees precise steps in the thickness growth of LbL self-assembled films, because only those attached with electrostatic