传感材料与传感技术丛书

Sensing Material and Sensing Technology Series

CHEMICAL SENSORS SIMULATION AND MODELING

Volume 5 Electrochemical Sensors

EDITED BY **GHENADII KOROTCENKOV**

影 印 版

化学传感器：仿真与建模

第 5 卷 电化学传感器

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PREFACE

This series, *Chemical Sensors: Simulation and Modeling,* is the perfect complement to Momentum Press's six-volume reference series, *Chemical Sensors: Fundamentals of Sensing Materials* and *Chemical Sensors: Comprehensive Sensor Technologies,* which present detailed information about materials, technologies, fabrication, and applications of various devices for chemical sensing. Chemical sensors are integral to the automation of myriad industrial processes and everyday monitoring of such activities as public safety, engine performance, medical therapeutics, and many more.

Despite the large number of chemical sensors already on the market, selection and design of a suitable sensor for a new application is a difficult task for the design engineer. Careful selection of the sensing material, sensor platform, technology of synthesis or deposition of sensitive materials, appropriate coatings and membranes, and the sampling system is very important, because those decisions can determine the specificity, sensitivity, response time, and stability of the final device. Selective functionalization of the sensor is also critical to achieving the required operating parameters. Therefore, in designing a chemical sensor, developers have to answer the enormous questions related to properties of sensing materials and their functioning in various environments. This five-volume comprehensive reference work analyzes approaches used for computer simulation and modeling in various fields of chemical sensing and discusses various phenomena important for chemical sensing, such as surface diffusion, adsorption, surface reactions, sintering, conductivity, mass transport, interphase interactions, etc. In these volumes it is shown that theoretical modeling and simulation of the processes, being a basic for chemical sensor operation, can provide considerable assistance in choosing both optimal materials and optimal configurations of sensing elements for use in chemical sensors. The theoretical simulation and modeling of sensing material behavior during interactions with gases and liquid surroundings can promote understanding of the nature of effects responsible for high effectiveness of chemical sensors operation as well. Nevertheless, we have to understand that only very a few aspects of chemistry can be computed exactly.

However, just as not all spectra are perfectly resolved, often a qualitative or approximate computation can give useful insight into the chemistry of studied phenomena. For example, the modeling of surface-molecule interactions, which can lead to changes in the basic properties of sensing materials, can show how these steps are linked with the macroscopic parameters describing the sensor response. Using quantum mechanics calculations, it is possible to determine parameters of the energetic (electronic) levels of the surface, both inherent ones and those introduced by adsorbed species, adsorption complexes, the precursor state, etc. Statistical thermodynamics and kinetics can allow one to link those calculated surface parameters with surface coverage of adsorbed species corresponding to real experimental conditions (dependent on temperature, pressure, etc.). Finally, phenomenological modeling can tie together theoretically calculated characteristics with real sensor parameters. This modeling may include modeling of hot platforms, modern approaches to the study of sensing effects, modeling of processes responsible for chemical sensing, phenomenological modeling of operating characteristics of chemical sensors, etc.. In addition, it is necessary to recognize that in many cases researchers are in urgent need of theory, since many experimental observations, particularly in such fields as optical and electron spectroscopy, can hardly be interpreted correctly without applying detailed theoretical calculations.

Each modeling and simulation volume in the present series reviews modeling principles and approaches particular to specific groups of materials and devices applied for chemical sensing. *Volume 1: Microstructural Characterization and Modeling of Metal Oxides* covers microstructural characterization using scanning electron microscopy (SEM), transmission electron spectroscopy (TEM), Raman spectroscopy, in-situ high-temperature SEM, and multiscale atomistic simulation and modeling of metal oxides, including surface state, stability, and metal oxide interactions with gas molecules, water, and metals. *Volume 2: Conductometric-Type Sensors* covers phenomenological modeling and computational design of conductometric chemical sensors based on nanostructured materials such as metal oxides, carbon nanotubes, and graphenes. This volume includes an overview of the approaches used to quantitatively evaluate characteristics of sensitive structures in which electric charge transport depends on the interaction between the surfaces of the structures and chemical compounds in the surroundings. *Volume 3: Solid-State Devices* covers phenomenological and molecular modeling of processes which control sensing characteristics and parameters of various solid-state chemical sensors, including surface acoustic wave, metal-insulator-semiconductor (MIS), microcantilever, thermoelectric-based devices, and sensor arrays intended for "electronic nose" design. Modeling of nanomaterials and nanosystems that show promise for solid-state chemical sensor design is analyzed as well. *Volume 4: Optical Sensors* covers approaches used for modeling and simulation of various types of optical sensors such as fiber optic, surface plasmon resonance, Fabry-Pérot interferometers, transmittance in the mid-infrared region, luminescence-based devices, etc. Approaches used for design and optimization of optical systems aimed for both remote gas sensing and gas analysis chambers for the nondispersive infrared (NDIR) spectral range are discussed as well. A description of multiscale atomistic simulation of hierarchical nanostructured materials for optical chemical sensing is also included in this volume. *Volume 5: Electrochemical Sensors* covers modeling and simulation of electrochemical processes in both solid and liquid electrolytes, including charge separation and transport (gas diffusion, ion diffusion) in membranes, proton–electron transfers, electrode reactions, etc. Various models used to describe electrochemical sensors such as potentiometric, amperometric, conductometric, impedimetric, and ion-sensitive FET sensors are discussed as well.

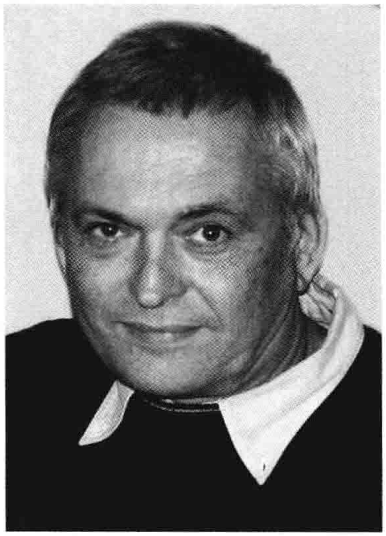
I believe that this series will be of interest of all who work or plan to work in the field of chemical sensor design. The chapters in this series have been prepared by well-known persons with high qualification in their fields and therefore should be a significant and insightful source of valuable information for engineers and researchers who are either entering these fields for the first time, or who are already conducting research in these areas but wish to extend their knowledge in the field of chemical sensors and computational chemistry. This series will also be interesting for university students, post-docs, and professors in material science, analytical chemistry, computational chemistry, physics of semiconductor devices, chemical engineering, etc. I believe that all of them will find useful information in these volumes.

G. Korotcenkov

About the Editor

Ghenadii Korotcenkov received his Ph.D. in Physics and Technology of Semiconductor Materials and Devices in 1976, and his Habilitate Degree (Dr. Sci.) in Physics and Mathematics of Semiconductors and Dielectrics in 1990. For a long time he was a leader of the scientific Gas Sensor Group and manager of various national and international scientific and engineering projects carried out in the Laboratory of Micro- and Optoelectronics, Technical University of Moldova. Currently, Dr. Korotcenkov is a research professor at the Gwangju Institute of Science and Technology, Republic of Korea.

Specialists from the former Soviet Union know Dr. Korotcenkov's research results in the field of study of Schottky barriers, MOS structures, native oxides, and photoreceivers based on Group III–V compounds very well. His current research interests include materials science and surface science, focused on nanostructured metal oxides and solid-state gas sensor design. Dr. Korotcenkov is the author or editor of 11 books and special issues, 11 invited review papers, 17 book chapters, and more than 190 peer-reviewed articles. He holds 18 patents, and he has presented more than 200 reports at national and international conferences.



Dr. Korotcenkov's research activities have been honored by an Award of the Supreme Council of Science and Advanced Technology of the Republic of Moldova (2004), The Prize of the Presidents of the Ukrainian, Belarus, and Moldovan Academies of Sciences (2003), Senior Research Excellence Awards from the Technical University of Moldova (2001, 2003, 2005), a fellowship from the International Research Exchange Board (1998), and the National Youth Prize of the Republic of Moldova (1980), among others.

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Contents

PART 3

ELECTROCHEMICAL BIOSENSORS

CHAPTER 7

Nanomaterial-Based Electrochemical Biosensors

N. Jaffrezic-Renault

1. INTRODUCTION

Nowadays nanotechnology is sharing knowledge, tools, techniques, and information with electrochemistry and electroanalysis in other fields. Nanobiomaterials are one of the very important products of nanotechnology. Nanobiomaterials can be obtained, in general, by either the controlled assembly of nanoscale building blocks (a bottom-up approach) or controlled elimination of starting materials and biomaterials to the nanoscale (a top-down approach).

Certain nanomaterials are attractive probe candidates because of their (1) small size (1–100 nm) and correspondingly large surface-to-volume ratio, (2) chemically tailorable physical properties, directly related to size, composition, and shape, (3) unusual target binding properties, and (4) overall structural robustness.

Nanomaterials such as nanoparticles or carbon nanotubes connected with biomolecules, in the same size order of magnitude, are being used for several bioanalytical applications. Electroanalysis is taking advantage of all the possibilities offered by nanomaterials which are easy to detect by conventional electrochemical methods (i.e., electroactive nanoparticles, etc.) or compatible with (bio)sensor building technologies.

The most important advantages that nanomaterials bring to electroanalysis are the following.

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1. Their immobilization on electrode surfaces generates a roughened conductive-high-surface-area interface that enables the sensitive electrochemical detection of molecular and biomolecular analytes.
2. They can act as effective labels for the amplified electrochemical analysis of the respective analytes.
3. The conductivity properties of metal nanoparticles enable the design of biomaterial architectures with predesigned and controlled electrochemical functions.

In this chapter, the state-of-the-art of nanomaterial-based electrochemical sensors will be presented, based on different bottom-up approach building technologies of nanomaterials, applied to different transducing techniques (amperometry, potentiometry, impedancemetry, and conductimetry), and to different biomolecules (enzymes, antibodies, DNA). Nanomaterials are classified as conducting nanomaterials (metallic nanoparticles such as gold nanoparticles and carbon nanotubes) and nonconducting nanomaterials such as magnetic nanoparticles (MNPs).

2. NANOMATERIALS: FABRICATION, CHEMICAL AND PHYSICAL PROPERTIES

2.1. CONDUCTING NANOMATERIALS

2.1.1. Metal Nanoparticles

Gold nanoparticles (AuNPs) can be prepared using an electron beam or through optical exposure. However, two more simple modes are generally preferred for the construction of electrochemical biosensors. In the first one, colloidal gold particles are prepared with a wide range of diameters and relatively high monodispersity by adding sodium citrate solution to a boiling $HAuCl_4$ aqueous solution (Katz et al. 2004). The size of the resulting colloidal gold nanoparticles, whose surfaces are negatively charged with citrate, is controlled by the molar ratio of $HAuCl_4$/sodium citrate (the lower the ratio, the smaller the particle size). The second method is based on the electrodeposition of gold nanoparticles from a $HAuCl_4$ solution onto the bulk electrode material (Rashid et al. 2006), and in this case experimental variables involved in the electrodeposition process (such as the applied potential and the time of deposition) govern the size and morphology of the nanoparticles formed.

Electrical properties of AuNPs have been characterized by physical measurements. Gold clusters stabilized by chemisorbed monolayers of octane-, dodecane- or hexadecanethiolate have been studied in the solid phase (Terrill et al. 1995). Films of the dry, solid cluster compound on interdigitated array electrodes exhibit