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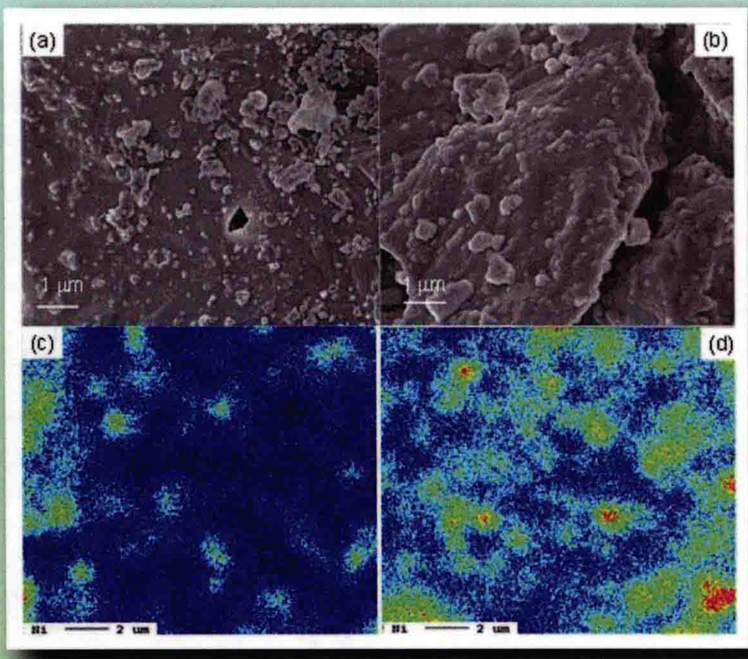
Interactions of Nanomaterials with Emerging Environmental Contaminants



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Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previous published papers are not accepted.

ACS Books Department

Preface

Emerging environmental contaminants are newly identified or previously unrecognized pollutants, which primarily include human and veterinary pharmaceuticals and personal-care products, surfactants, plasticizers, flame retardants, metals and metalloids, various industrial additives, pesticides, and pesticide metabolites. The use of novel nanomaterials with unique characteristics has been demonstrated to increase the removal efficiency of emerging pollutants, which provides a promising strategy to control the distribution of environmental contaminants. In addition, nanomaterials also can serve as ideal platforms for precise and accurate detection and sensing of emerging contaminants in the environment and biological fluids; this is because of their novel characteristics on optical and electrochemical properties. The interactive research of nanomaterials with emerging environmental contaminants will improve our understanding of the implication and application of nanomaterials in the environment.

This book is derived from the symposium "*Interactions of Nanomaterials with Emerging Environmental Contaminants*" at the 244th ACS National Meeting in Philadelphia during the fall of 2012 sponsored by the American Chemical Society (ACS) Division of Environmental Chemistry. Many topics addressing issues of interaction of emerging environmental pollutants with nanomaterials (including physical, photochemical, and biological interactions) were presented in this symposium, and they constitute the main content of this book.

This book contains 12 peer-reviewed chapters that cover various aspects of interaction of various nanomaterials with environmental contaminants. These chapters can be organized into two major sections: (I) interaction of nanomaterials with biomolecules for biosensing and detection of contaminants (Chapter 1-4) and (II) interaction of nanomaterials with contaminants to enhance the removal efficiency and rate of emerging pollutants (Chapter 5-12). Chapter 1 by Ren, Zang, Qie, and Baker provides an overview of the adjuvant effect of emerging nanomaterials. The nanoparticles can serve as drug delivery to deliver antigens to species targets. In contrast, ambient nanoparticles exhibit adverse effect on human and ecological health. To address the accurate and precise detection of environmental contaminants in the environment (as well as in the human body), Chapter 2 and Chapter 3 have developed photoluminescent gold nanomaterials — including gold nanoparticles and gold nanodots — for the monitoring and detection of metal ions, proteins, and bacteria in an aquatic ecosystem. In Chapter 2, Unnikrishnan and Huang have synthesized luminescent core-shell Au nanodots using different kinds of capping ligands (including alkanethiols, proteins, DNA, thiol derived carbohydrates, and aptamers) as the shell layer for detection and determination of mercury ions, proteins, and *E. coli*. Chang and his team (Chapter 3) have developed several functional Au nanoparticles and Au nanodot-based sensors that allow the sensitive and selective detection of mercury, lead, and copper ions through analytes induced changes in colors, absorption, and fluorescence. In addition, a biosensing system (AlGaN/GaN high electron mobility transistors immobilized with antibodies) is developed by Wang and his team (Chapter 4) to effectively detect a short peptide only containing 20 amino acids, which opens a door for investigation into nanomaterials with biomolecules.

The applications of nanomaterials for various reactions (including adsorption, photocatalytic degradation, and reductive dechlorination) are also addressed. Huang, Padhye, and Wang (Chapter 5) describe the generation of N-nitrosamines from transformation of amines catalyzed by activated carbons. This interaction is important because activated carbon and amine are often used in water treatment plants. In Chapter 6, Du and Jing explore the dynamic adsorption process of propranolol at the TiO_2/water interface on the molecular level. In addition to adsorption behavior, Hung and his colleagues (Chapter 7) combine TiO_2 and carbon nanotubes to adsorb and look at the photocatalytic decomposition of bisphenol A, which is an endocrine disrupting chemical widely existing in the environment.

Iron-based nanomaterials are effective catalysts for the removal of emerging pollutants in the environment. Ren, Han, Al Anazi, Nadagouda, and Dionysiou (Chapter 8) discuss the application of different iron-based nanomaterials for environmental remediation — including water treatment, groundwater remediation, and soil decontamination. Ferrate, ferrites, and TiO_2-composite magnetic iron oxides are used for the removal of contaminants of emerging pollutants. In addition to iron oxide catalysts, zerovalent metals are also common nanomaterials widely used for reduction of emerging pollutants. Su, Tso, Peng, and Shih (Chapter 9) have used nanoscale zerovalent iron (nZVI) and bimetallic Pd/Fe as the dual functional tools for adsorption and reduction of aromatic contaminants (including decabrominated diphenyl ether, hexachlorobenzene, penrachlorophenol, and Congo red). The combination of biological or sequential Fenton treatment on the mineralization of some emerging contaminants is also evaluated in this chapter. In Chapter 10, McPherson, Goltz, and Agrawal summarize the role of polyelectrolyte stabilization and catalytic metal modification in the enhanced performance of nZVI. The addition of polyelectrolyte stabilizers to nZVI decreases particle agglomeration and reduces particle size — resulting in the increase in reactivity and transport in porous media. The modification of nZVI with Pd and Ni for the enhancement of reactivity is also summarized and discussed. In addition, three field studies using Pd-nZVI for the remediation of chlorinated compounds in groundwater are introduced. Sharma, Siskova, and Zboril (Chapter 11) review the recent development of nanoscale zerovalent iron and magnetic bimetallic Fe/Ag nanoparticles with core-shell structures. They also show the usefulness of these nanomaterials on nutrient removal, transformation of halogenated aromatic contaminants, and antimicrobial activity. In addition to zerovalent iron, Lee and Doong (Chapter 12) have demonstrated the feasibility of using another environmentally friendly metal to remove chlorinated compounds. In this chapter, the authors review and discuss the reductive dechlorination of chlorinated hydrocarbons and emerging pollutants by zerovalent silicon and bimetallic Fe/Si and Ni/Si. More importantly, they demonstrate the synergistic effect of nickel ions and polyethylene glycol on the dechlorination rate.

The understanding of interaction of emerging contaminant with various nanomaterials is essential to exploring the applications of nanotechnology in the environment. We hope that this collection will benefit graduate students who are engaged in research and development in the advancement of nanotechnology and environmental science and technology. We wish to thank Anne Brenner and Timothy Marney of the editorial department of ACS for their assistance in preparing this volume and for keeping us on schedule.

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Interaction of Nanomaterials with Biomolecules for Biosensing

Chapter 1

The Adjuvant Effect of Emerging Nanomaterials: A Double-Edged Sword

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[†]This manuscript is in memory of my advisor and friend, Dr. Gregory L. Baker who passed away unexpectedly while this paper was being written.

Nanoparticles have growing applications in industry, consumer products, biology and medicine. One of those applications involves the interaction between nanoparticles and immune components. The nanoparticles can act as antigen carriers to deliver and release antigens to specific targets, and enhance the immune response against a variety of antigens as adjuvants. The adjuvant effects of nanoparticle size, shape, surface charge, linkage method on the immunological response are also discussed. In contrast, as-prepared nanomaterials and ambient particulate matter (PM) from air pollution exhibit adverse adjuvant effect *in vitro* and *in vivo*, and recent advances to address their potential risk on human health are also included in this review.

Introduction

Nanomaterials are characterized by their sizes which are in the range of several nanometers to several hundreds of nanometers, well below the micrometer range. Because of their nanoscale dimensions and hence large specific surface area, nanomaterials exhibit remarkable physicochemical properties, such as optical property (*1*), catalytic property (*2*), mechanical property (*3*) and drug delivery property (*4*), which are usually not active for their bulk materials. Due to these specific properties, research and development of new nanomaterials have steadily increased, which can be reflected by the increasing number of publications on nanomaterials research, from about 110 publications in 1990 to 4200 publications in 2000 followed by a burst to more than 77900 publications in 2013 (key word: nano, ISI web of knowledge, 05/2013). As a result, nanomaterials, rapidly introduced into electronic devices, construction and composite materials, are more and more present in workplaces as well as consumer products since large-scale producing, handling and processing facilities of nanomaterials are easily available.

Although properties of nanomaterials are impressive from physicochemical viewpoint, they also raise safety concerns of nanomaterials. One major concern is that nanomaterials may lead to potential toxic effect on environment or human health, because nanomaterials readily penetrate cell membranes, travel throughout the body, and deposit in target organs. Therefore, it may trigger injurious responses (*5*, *6*). In recent years, nanotoxicology has become one of the major research focuses in nanoscience. While the number of publications dealing with nanotoxicity study was about 1350 in 2000, this increased to 5500 in 2010, then it rapidly jumped to more than 8200 in 2013 (key words: particle/toxicity, ISI web of knowledge, 05/2013). These clearly indicate that nano toxicology has been widely recognized and gained more and more attention. These studies would help to determine whether and to what extent these properties may present a threat to environment and human beings, and guide applications of nanomaterials in daily life as well (*7*). Among several mechanisms proposed to explain the adverse effect of nanomaterials, generation of reactive oxygen species and oxidative stress has received the most attention (*8*). Dimension, surface chemistry, surface charge and aggregation of nanomaterials are related to their nanotoxicity (*5*). It is difficult to identify the health risk of each new nanomaterials because all material properties need to be taken into account during the toxicity study.

Despite safety concerns that nanomaterials could present adverse effect on human beings, it has been reported that nanomaterials serving as effective vaccine/drug carriers could improve and/or facilitate the extended release of antigens, and hence enhance the immune response level and quality of antigens (*9*, *10*). This has drawn more and more research focuses worldwide in nanomedicine field, especially in vaccine immunology, and nanomaterial has been referred as nano adjuvant to enhance the immunogenicity of specific vaccine or antigen. From ISI web of knowledge (key words: particle/adjuvant, 05/2013), there were only 380 publications on nano-adjuvant research in 2000 and it increased to more than 1350 in 2010, and then rapidly jumped to more than 1800 publications in 2013.