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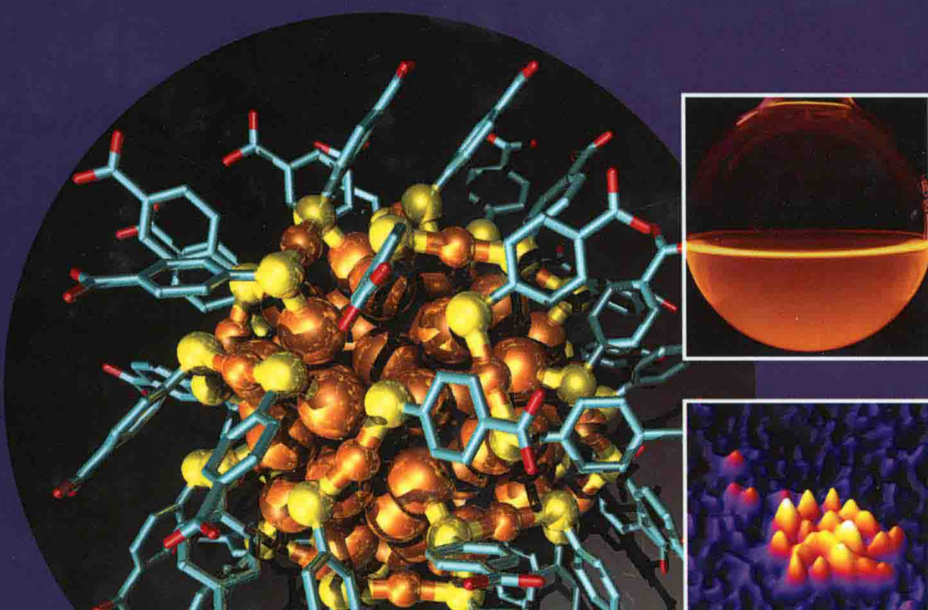
Volume 9

Protected Metal Clusters: From Fundamentals to Applications



Edited by
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Protected Metal Clusters: From Fundamentals to Applications

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Protected Metal Clusters: From Fundamentals to Applications

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Tatsuya Tsukuda/Tokyo, Japan
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Contents

Chapter 1

Introduction

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Chapter Outline

1.1 PROTECTED METAL CLUSTERS: A BRIEF HISTORY

Metal clusters composed of less than a few hundred atoms are located between the bulk and atomic states of the corresponding metal and have attracted physicists over the last four decades. The central subject of the early stage of the cluster research was to observe the finite-size effects on physical properties of metal clusters and to understand their microscopic origins. Development of new experimental and theoretical methods has led to a discovery of a variety of remarkable size-specific phenomena and physicochemical properties. For example, the development of versatile methods of cluster production such as laser ablation coupled with mass spectrometry has unveiled magic numbers of clusters due to the closure of electronic and/or geometric structure(s).[1] These observations have led to the establishment of the concepts of electron shell closing based on the jellium model[2] and superatoms.[3] It has been widely recognized that various physicochemical (magnetic, optical, chemical, and thermal) properties of metal clusters deviate significantly from their bulk counterparts and evolve dramatically as a function of size, as exemplified by the metal—insulator transition.[4] During this development, the community has come to be convinced that metal clusters are promising functional units of

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novel materials and has made an effort to develop cluster-based materials under catchphrases: "small is different"[5,6] and "every atom counts."[7,8]

Chemical synthesis has been a challenge to be overcome to initiate, accelerate, and deepen materials science of metal clusters, as evidenced by the explosive growth in materials science of nanocarbons after the large-scale production of C_{60}.[9] In the field of inorganic chemistry, phosphine-protected small Au cluster compounds have been long studied with a special focus on the synthesis and structural determination. One of the most famous examples is Schmid's Au_{55} compound.[10] However, variation of the systems and scope of the application were limited due to the instability and structural and compositional ambiguity. It was in 1994, when the first chemical synthesis of thiolate (RS)-protected Au nanoparticles was reported by Brust and Schiffrin.[11] This simple but inventive method allowed us to treat the metal clusters as conventional chemical compounds. In the late 1990s, these monolayer-protected clusters have been viewed as *nanocrystal gold molecules* by Whetten[12] and *gold nanoelectrode* by Murray.[13,14] The structure models based on hollow-site or bridge-site absorption of thiolates on nanocrystals have been theoretically developed by Landman.[15] Garzón was the first who suggested a strong deformation of the core structure by the thiolate adsorption.[16] Häkkinen proposed a concept of "divide and protect"[17] in which the Au clusters are protected by Au—thiolate oligomers. The first report on the mass spectrometric determination of molecular formula of $Au_n(SR)_m$ in 2005 by Tsukuda has opened a door to the atomically precise synthesis.[18] In 2007, Kornberg made a breakthrough in structure determination of protected metal cluster ($Au_{102}(SR)_{44}$) using single crystal X-ray diffractions.[19] Research interest in basic science and practical applications of the ligand-protected metal clusters has been explosively growing in the last decade, including many other ligand types than thiols and many other metals than gold.[20–44]

1.2 THE AIMS OF THE BOOK

It is an opportune moment after 20 years since the first report on the wet chemical synthesis to write a book concerning ligand-protected clusters in order to provide vivid snapshots of current research trends and innovative applications. This book entitled *Protected Metal Clusters: From Fundamentals to Applications* is included in a series entitled "Frontiers of Nanoscience (Elsevier; series editor, Richard Palmer)" and is aimed to survey development in the last decade in the fundamental concepts and potential applications of atomically precise metal clusters protected by organic ligands. This class of materials is now emerging due to breakthroughs in synthesis and characterization that have taken place during the last few years. This book on these exciting novel nanomaterials has two major aims depending on the audience. It is not trivial for the students and newcomers in this research field to systematically understand the fundamentals from a huge body of literature. Thus the