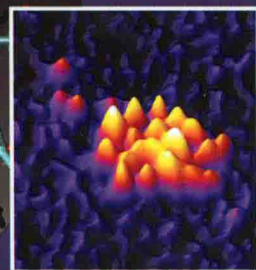
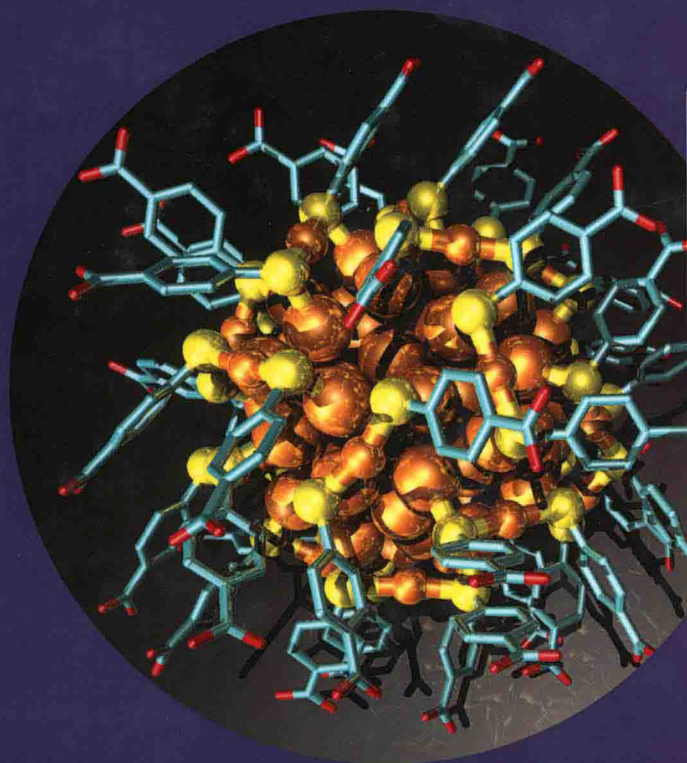




Frontiers of Nanoscience
Series Editor: Richard E. Palmer

Volume 9

Protected Metal Clusters: From Fundamentals to Applications



Edited by
Tatsuya Tsukuda
Hannu Häkkinen

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Protected Metal Clusters: From Fundamentals to Applications

Edited by

Tatsuya Tsukuda

Department of Chemistry,
School of Science,
The University of Tokyo, Tokyo, Japan

Hannu Häkkinen

Departments of Chemistry and Physics,
Nanoscience Center,
University of Jyväskylä,
Jyväskylä, Finland



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ISBN: 978-0-08-100086-1

ISSN: 1876-2778

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Frontiers of Nanoscience

Volume 9

Protected Metal Clusters: From Fundamentals to Applications

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Contributors

Christopher J. Ackerson, Department of Chemistry, Colorado State University, Fort Collins, CO, USA

Christine M. Aikens, Department of Chemistry, Kansas State University, Manhattan, KS, USA

Yuxiang Chen, Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, USA

Nirmal Goswami, Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore

Hannu Häkkinen, Department of Physics, and Department of Chemistry, Nanoscience Center, University of Jyväskylä, Jyväskylä, Finland

De-en Jiang, Department of Chemistry, University of California, Riverside, CA, USA

Rongchao Jin, Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, USA

Wataru Kurashige, Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Shinjuku-ku, Tokyo, Japan

Jingguo Li, Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore

Yuichi Negishi, Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Shinjuku-ku, Tokyo; Photocatalysis International Research Center, Tokyo University of Science, Noda, Chiba; and Department of Materials Molecular Science, Institute for Molecular Science, Okazaki, Aichi, Japan

Thomas W. Ni, Department of Chemistry, Colorado State University, Fort Collins, CO, USA

Yoshiki Niihori, Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Shinjuku-ku, Tokyo, Japan

Richard E. Palmer, Nanoscale Physics Research Laboratory, School of Physics and Astronomy, University of Birmingham, Birmingham, UK

Shinjiro Takano, Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku, Tokyo, Japan

Qing Tang, Department of Chemistry, University of California, Riverside, CA, USA

Marcus A. Tofanelli, Department of Chemistry, Colorado State University, Fort Collins, CO, USA

Tatsuya Tsukuda, Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku, Tokyo; Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto, Japan

Yu Wang, Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China

Zhi Wei Wang, Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing, China

Jianping Xie, Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore

Huayan Yang, Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China

Nanfeng Zheng, Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, China

Acknowledgments

We would like to express our appreciation to Professor Richard Palmer (Birmingham University), the series editor of **Frontiers of Nanoscience**, for giving us an opportunity to edit a book on the currently hot topic of nanomaterials. We are grateful to all our colleagues for their significant efforts in writing the chapters. We thank our Editorial Project Manager, Derek Coleman (Amsterdam), and Acquisitions Editor, Susan Dennis (Oxford), for their guidance and patience throughout this project. H.H. thanks the Wihuri Foundation for supporting a sabbatical leave during which part of this project was completed.

June 2015

Tatsuya Tsukuda/Tokyo, Japan

Hannu Häkkinen/Jyväskylä, Finland

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Chapter 1

Introduction

Tatsuya Tsukuda^{*,§,1} and Hannu Häkkinen^{‡,†}

^{*}Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku, Tokyo, Japan;

[§]Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Katsura, Kyoto, Japan; [‡]Department of Physics, Nanoscience Center, University of Jyväskylä, Jyväskylä, Finland; [†]Department of Chemistry, Nanoscience Center, University of Jyväskylä, Jyväskylä, Finland

¹Corresponding author: E-mail: tsukuda@chem.s.u-tokyo.ac.jp

Chapter Outline

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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 model² 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

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 C₆₀.⁹ 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 Au₅₅ 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 Whetten¹² 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 (Au₁₀₂(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