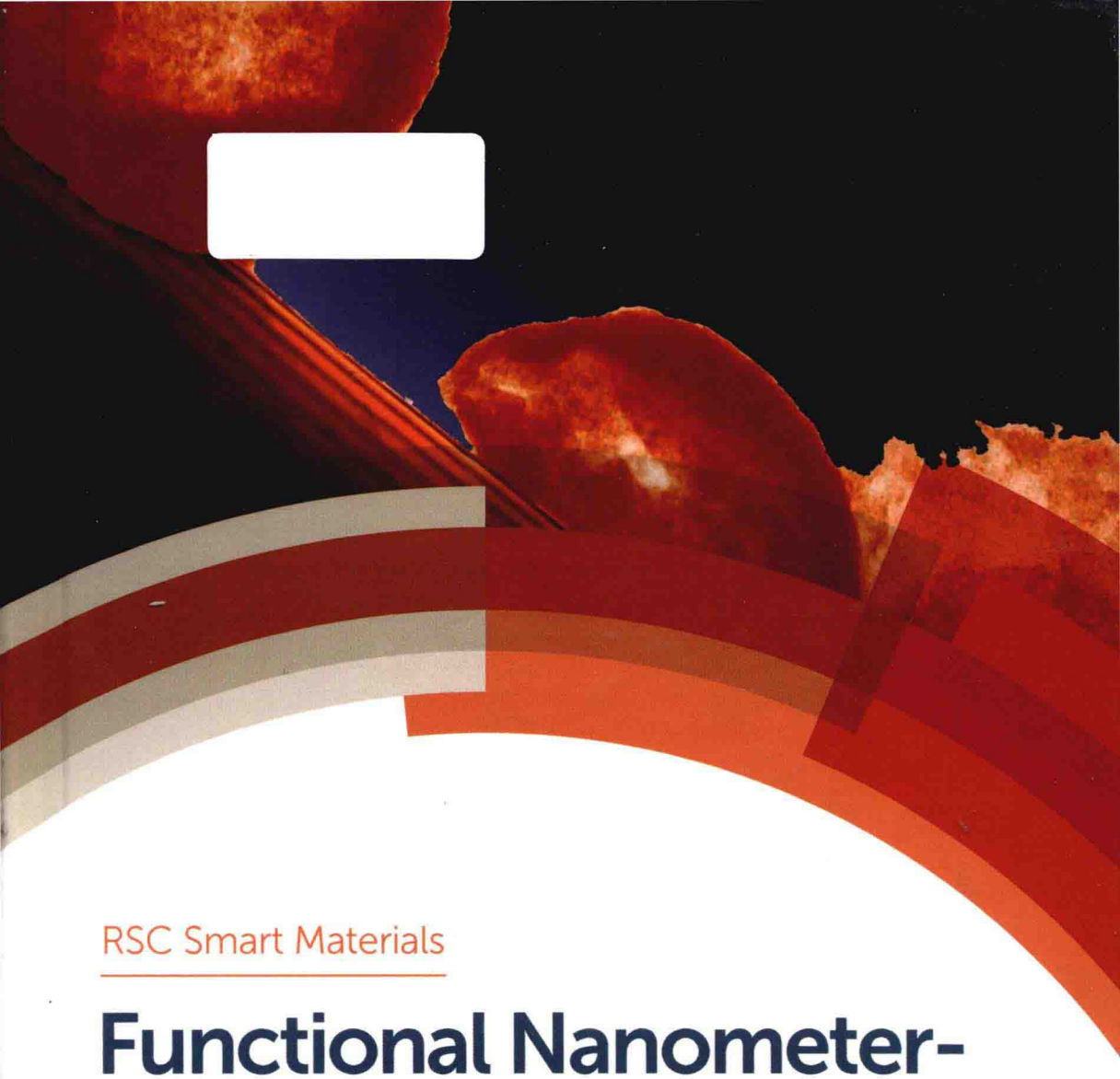

RSC Smart Materials

Functional Nanometer-Sized Clusters of Transition Metals

Synthesis, Properties and Applications

Edited by Wei Chen and Shaowei Chen

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Functional Nanometer-Sized Clusters of Transition Metals
Synthesis, Properties and Applications

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Preface

Metal nanocrystals in the size range of 1 to 100 nm have attracted extensive attention in the past decades due to their unusual properties and potential applications in many areas. In particular, metal clusters with a core size smaller than 2 nm exhibit unique physical and chemical properties that are significantly different from those of the corresponding large nanoparticles and molecular compounds. Such a size range represents a bridge between atoms/molecules and nanoparticles, and thus represents a fascinating multidisciplinary research area. Yet, because of the ultrasmall dimensions, development of effective protocols for the size-controlled synthesis has been a significant challenge in the studies of metal nanoclusters. In recent years, various effective strategies have been described in the literature for the synthesis of metal nanoclusters with a specific number of metal atoms and surface protecting ligands. The successful preparation of composition-determined metal clusters renders it possible to study their size- and composition-related properties. Significantly, with a size comparable to the Fermi wavelength of electrons and consequently the formation of discrete electronic energy levels, metal nanoclusters exhibit unprecedented optical and electronic properties, including size-dependent energy level structures, photoluminescence, and catalytic properties. Therefore, metal nanoclusters have been found to show promising applications in nanoelectronics, catalysis, biological and chemical sensing, molecular imaging, biological labeling, biomedicine, and so on.

This book highlights some recent progress in the synthesis, characterization, interfacial engineering and applications of metal nanoclusters. The contributors to this book consist of leading experts in this field. For organothiol-stabilized metal nanoclusters, the mechanism of cluster formation is of critical importance to achieve structure-controlled synthesis. Tong and

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co-workers first review and discuss the relevant chemistry involved in the two-phase synthesis of alklychalcogenolate-stabilized metal nanoparticles. As an important research field of metal nanoclusters, González and López-Quintela summarize the recently developed strategies and synthetic routes for the preparation of photoluminescent atomic quantum clusters. Up to now, the research in the field of metal nanocluster is mainly concentrated on gold and silver metals. In this book, several chapters focus on Au and Ag nanoclusters. Bigioni *et al.* report the magic-number silver nanoclusters, Xu and Suslick summarize the work on water-soluble fluorescent silver nanoclusters, Yang and Wang highlight biomolecule-protected silver nanoclusters, Xie *et al.* present the newly-developed synthetic strategies, and Pradeep *et al.* discuss in detail the preparation and application of noble metal clusters in protein templates. As an important application of metal nanoclusters, López-Quintela *et al.*, Lu and Chen, and Tsukuda *et al.* review the catalytic properties of metal nanoclusters from different aspects. Wang and Ubaldo give a summary of the development of In Silico study of metal nanoclusters, which is helpful for the experimental syntheses and design of metal clusters. Zhou and Dong and Tanaka and Inouye highlight the biological applications of metal nanoclusters. Chen *et al.* review the recent advances in Janus nanoparticles through interfacial engineering. The editors express their deep appreciation to the authors for their support and contributions to the book.

This book will be a valuable reference for researchers in the general area of functional nanomaterials. It may also serve as a study guide for graduate students and senior undergraduate students who are interested in nanoscale materials chemistry and engineering.

Wei Chen
Shaowei Chen

Contents

RSC Smart Materials No. 7
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CHAPTER 1

Mechanistic Insights into the Brust–Schiffrin Synthesis of Organochalcogenolate-Stabilized Metal Nanoparticles

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1.1 Introduction

Metal nanoparticles (NPs) made of tens, hundreds, or thousands of atoms can have tunable chemical and physical properties as a function of NP size (number of atoms), elemental composition, and/or chemical environment (ligand-stabilized, matrix-embedded, or structurally-encaged). These NPs are artificial atoms[1–7] and novel building blocks for new materials that hold novel physicochemical properties as compared to the existing (atomic/molecular) materials. It is expected that these novel materials will enable widespread technological breakthroughs in the not too distant future, for instance in molecular and/or nano-electronics and clean energy generation.[8,9] Within this broad context, organoligands, particularly organothiolate-stabilized metal (mainly Au) NPs, have been subjected to intensive

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research over the last two decades due to their potential applications in nano-optics,[10] nano-electronics,[11] (bio)sensing[12] and medicinal science (theranostics).[13]

The first step towards any practical applications of metal NPs is the synthesis of these metal NPs, preferably air-stable and of homogeneous size distribution and known chemical composition. Among many synthetic methods, the *B*rust–*S*chiffrin two-phase *m*ethod (BSM) synthesis worked out by Brust, Schiffrin, and company in 1994,[14] including its late variants, is definitively the most widely employed synthetic approach to make <5 nm organo-ligand-stabilized metal NPs. Briefly, a typical BSM consists of three steps: Step 1, metal ions are phase transferred (PT-ed) from an aqueous to an organic phase (usually toluene or benzene) with a PT reagent (usually tetraoctylammonium bromide (TOAB), *i.e.* R_4NBr, $R = C_8H_{17}$). Step 2, organochalcogen-containing ligand (usually RSH) is added to the separated organic phase during which Au^{III} cations can be reduced to Au^{I} cations. Step 3, metal ions residing in the separated organic phase are reduced into M^0 by a reducing reagent like $NaBH_4$ during which organochalcogenolate-protected metal NPs are formed.

Despite the prevailing use of the BSM in the synthesis of sub-5 nm metal (mainly Au) NPs (according to Thomson Reuters' Web of Knowledge, the original paper[14] has accumulated a current number of citations as high as 3755, and counting), mechanistic details of the BSM synthesis have been sketchy until very recently.[15–18] A long-held belief concerning the metal precursor in the synthesis of metal NPs, probably due to earlier papers by Whetten *et al.*,[19,20] has been that the metal-thiolate polymer, $[Au^{I}SR]_n$, is the metal ion precursor of metal NPs. However, a recent paper by Goulet and Lennox[18] has shown that the metal–TOA^+ complex, $[TOA][Au^{I}Br_2]$, can also be the major metal ion precursor. Our ensuing studies have not only confirmed the results of Goulet and Lennox, but also proposed that the BSM synthesis is an inverse micelle based approach based on their proton NMR results and showed *via* Raman spectroscopic study that the Au–S bond does not form until the formation of Au NPs.[15] In this chapter, we will review and discuss in various degrees of detail the relevant chemistry involved, particularly the role of encapsulated water, in the BSM synthesis of alkylchalcogenolate-stabilized metal NPs unravelled after the paper of Goulet and Lennox[18] and highlight the similarity and difference when ligands containing different chalcogen elements (S, Se, or Te) are used as the starting source of the NP-stabilizing agents.

1.2 Phase Transfer of Metal Ions: Formation of Inverse Micelle Encapsulated Water

1.2.1 Proton NMR Evidence of Encapsulated Water

The experimental evidence of possible encapsulated water by TOAB in an organic phase came first from the observation of a large down-field shift