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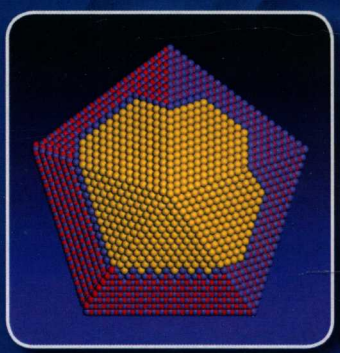
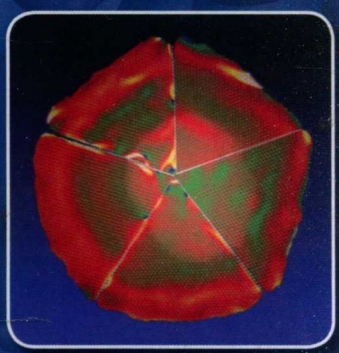
Nanoalloys

From Fundamentals to Emergent Applications





Edited by Florent Calvo

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Florent Calvo
CNRS and University of Lyon, France

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Nanoalloys

Foreword

Matter at the nanoscale exhibits some remarkable and unexpected properties that differ sharply from the behavior of bulk materials. For example, science students have been taught for centuries that gold is a "noble metal," that is, that it is very unreactive. However, nanoparticles of gold turn out to be extremely effective catalysts, for reasons that are only now beginning to be understood. Another remarkable example is the melting behavior of clusters of about 100 atoms of gallium or of tin. Since the mid-nineteenth century, we have understood that small particles melt at lower temperatures than their bulk counterparts, but these specific nanoparticles totally violate that dogma, and melt at temperatures higher than the corresponding bulk melting points. In short, even homogeneous metal nanoparticles are a fascinating and challenging form of matter that we are only in first stage of understanding.

Metal alloys at the nanoscale are an even more dramatic challenge. The variability of their composition and structure, the dependence of their behavior on those characteristics and the size of the nanoparticle, present us with a complexity, and, at the same time, a capacity to control properties, that we perhaps have never seen in any other form of matter. Most biomolecules are very complex, but making small changes in their composition or structure typically prevents them from functioning. Metal alloy nanoparticles can be changed a little in composition or structure and may well have only slightly altered properties—or may undergo very significant changes in behavior. We are just beginning to understand the nature of bonding in these systems, and of their kinetic behavior. As we learn more, and learn to control their composition, size and structure, we will develop the capability to make nanoscale devices with capabilities that are still unforeseen. This book describes how this field, potentially both deep in fundamentals and broad in applicability, is opening.

This book addresses the full range of the subject of nanoalloys. The first two chapters deal with their controlled synthesis, a major challenge. The next two address the theoretical and experimental approaches to understanding the electronic and geometric structures of nanoalloys. Then a series of chapters examine their properties—thermodynamic, kinetic, optical and magnetic, and then their behavior as catalysts. The penultimate chapter examines nanoalloys' roles in living organisms, and the final chapter discusses their use as building blocks in composite systems.

R. Stephen Berry

Contributors

Victor Abdelsayed Department of Chemistry, Virginia Commonwealth University, Richmond, VA, USA

Andrés Aguado Departamento de Física Teórica, Atómica y Óptica, Universidad de Valladolid, Valladolid, Spain

Giovanni Barcaro CNR-IPCF, Istituto per I Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche, Pisa, Italy

Dominique Bazin Laboratoire de Physique des Solides, Université Paris-Sud (XI), France; Laboratoire de Chimie de la Matière Condensée de Paris Université Pierre et Marie Curie et Collège de France, Paris, France

H. Brune Ecole Polytechnique Fédérale de Lausanne (EPFL), Insitute of Condensed Matter Physics (ICMP), Lausanne, Switzerland

E. Cottancin Université de Lyon, Université Lyon 1, CNRS, Laboratoire de Spectrométrie Ionique et Moléculaire (U.M.R. 5579) 43, Villeurbanne Cedex, France

A. Courty Laboratoire des Matériaux Mésoscopiques et Nanométriques (UMR7070), Université Pierre et Marie Curie–Paris 6, Paris, France

J. Dorantes-Dávila Instituto de Física, Universidad Autónoma de San Luis Potosí, San Luis Potosí, Mexico

M.S. El Shall Department of Chemistry, Virginia Commonwealth University, Richmond, VA, USA; Department of Chemistry, King Abulaziz University, Jeddah, Saudi Arabia

Ioana Fechete Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, Strasbourg, France

Riccardo Ferrando Dipartimento di Fisica dell'Università di Genova, Dodecaneso, Genova, Italy

Alessandro Fortunelli CNR-IPCF, Istituto per I Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche, Pisa, Italy

François Garin Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, Strasbourg, France

Miguel José–Yacamán Department of Physics and Astronomy, University of Texas at San Antonio, One UTSA Circle, San Antonio, TX, USA

Zbigniew Kaszkur Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

Fumitaka Mafuné Department of Basic Science, School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo, Japan

Karrina McNamara Department of Physics & Energy, Materials and Surface Science Institute, University of Limerick, Limerick, Ireland

Sergio Mejía-Rosales Center for Innovation and Research in Engineering and Technology, and CICFIM-Facultad de Ciencias Físico-Matemáticas, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, Nuevo León, Mexico

Ken Miyajima Department of Basic Science, School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo, Japan

Sherif Moussa Department of Chemistry, Virginia Commonwealth University, Richmond, VA, USA,

Fabio R. Negreiros CNR-IPCF, Istituto per I Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche, Pisa, Italy

G.M. Pastor Institut für Theoretische Physik, Universität Kassel, Kassel, Germany

M. Pellarin Université de Lyon, Université Lyon 1, CNRS, Laboratoire de Spectrométrie Ionique et Moléculaire (U.M.R. 5579) 43, Villeurbanne Cedex, France

C. Petit Laboratoire des Matériaux Mésoscopiques et Nanométriques (UMR7070), Université Pierre et Marie Curie–Paris 6, Paris, France

Arturo Ponce Department of Physics and Astronomy, University of Texas at San Antonio, One UTSA Circle, San Antonio, TX, USA

V. Repain Laboratoire Matériaux et Phénomènes Quantiques (UMR 7162), Université Paris Diderot-Paris 7, Paris, France

Luca Sementa CNR-IPCF, Istituto per I Processi Chimico-Fisici del Consiglio Nazionale delle Ricerche, Pisa, Italy

Mushtaq Ahmed Sobhan Department of Basic Science, School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo, Japan

Syed A.M. Tofail Department of Physics & Energy, Materials and Surface Science Institute, University of Limerick, Limerick, Ireland

Introduction

The last decade has seen a booming development of nanosciences, which now stand as their own field across physics, material sciences, chemistry and medicine. Nanoscale objects include organic particles such as fullerenes, carbon nanotubes or even graphene, semiconducting devices such as quantum dots for electronic or photonic applications, and even hydrogen-bonded compounds like water droplets for their relevance as nucleation seeds in atmospheric processes. The interplay between atomic and electronic structures makes metal nanoparticles highly versatile, already with many uses as catalysts, magnetic devices or optical probes. Although dating back to the mid nineteenth century and their discovery by Faraday, nanoparticles have become a major scientific topic when researchers gained the ability to synthesize them and, more importantly, to observe and understand their fascinating properties.

The most distinctive feature of nanoscale materials is the size dependence often displayed by these properties. Size dependence is usually quantitative: the optical response, the catalytic reactivity, or the magnetic moment exhibit variations that vary with the nanoparticle size, smoothly at first in the so-called scalable regime, then nonmonotonically when the particle becomes small enough. Under some circumstances, the dependence is more qualitative and can arise from some changes in chemical bonding. Besides its size, the shape of a nanoparticle can also affect its property, opening interesting avenues of research, e.g. in the design of photoelectronic devices such as nanoantennas.

Mixing several metals together provides another opportunity for tuning a physical or chemical property at the nanoscale. This ambition is rooted in the achievements of early metallurgists from the Bronze age who found several millennia ago that the strength and durability of their materials could be enhanced by mixing different metals. Metal alloys at the nanoscale are a prime example of nanoalloys in which the relative composition is a new variable to be varied, expectantly having a profound influence on the desired property along with size itself. However, it should be made clear here that nanoalloys do not only refer to mixed, nanoscale alloys. For sake of a general definition (and perhaps by lack of a more rigorous term), nanoalloys are currently understood as multimetallic nanoparticles, with no assumption about the chemical order within them. Fully phase-separated particles, such as core/shell compounds, represent an important class of nanoalloys, among other possible arrangements.

Adding the dimension of composition to the existing roles of size and structure entails a significant complexity, which could only be addressed after research on pure

metal nanoparticles had reached some level of maturity. Tackling this complexity by experimental or theoretical means requires dedicated tools that build upon methods available for monometallic systems, as well as methods more specific to the presence of several metals. One first objective of the present book is to provide a broad introduction to such methods, either for synthesis purposes or for fundamental investigations. Beyond fundamentals, and although a relatively young discipline, nanoalloys have also started to receive a considerable attention for their potential interest in several applied fields, for energy production, magnetic storage, or biomedicine. These topics are closely related to specific chemical or physical issues but deserved dissertations of their own.

This book was designed with the aim to present and discuss the major topics of relevance for nanoalloys, at a time where literature on the subject remains scarce. A particular attention was paid to both experimental and theoretical aspects, under the form of broad reviews that cover the most recent advances. The book is organized into 11 chapters covering the most fundamental aspects of nanoalloys related to their synthesis (Chapters 1 and 2) and characterization (Chapter 4), as well as their theoretical study (Chapter 3). Aspects related to their thermodynamics (Chapter 5) and kinetics (Chapter 6) are covered as well. The gear then moves to more specific topics, including optics (Chapter 7), magnetism (Chapter 8), and catalysis (Chapter 9), and finally to biomedical applications (Chapter 10) and the technologically relevant issue of self-assembly (Chapter 11).

The contributors of the book are all world experts in their respective fields, and it is a pleasure to thank them for their fine work. Prof. R. Stephen Berry, who has pioneered the study of the physics and chemistry of atomic clusters, is also gratefully acknowledged for his foreword.

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Florent Calvo

Contents

1 Chemical synthesis of metal nanoparticles and nanoalloys

Sherif Moussa, Victor Abdelsayed*, M.S. El Shall*,†*

*Department of Chemistry, Virginia Commonwealth University, Richmond, VA, USA, †Department of Chemistry, King Abulaziz University, Jeddah, Saudi Arabia

Chapter Outline

1.1 Introduction

It is now well established that nanoparticles (1–100 nm) exhibit unique chemical and physical properties that differ from those of the corresponding bulk materials [1–7]. The dependence of the properties of nanoscale materials on the size, shape and composition of the nanocrystal is a phenomenon of both fundamental scientific interest and many practical and technological applications [1–5]. These properties are often different, and sometimes superior, to those of the corresponding bulk materials.

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The origins of the differences can be explained by the high surface-to-volume ratio, dispersion factors and the quantum size effects unique to a specific length scale [1–7]. For example, semiconductor nanoparticles in the size range of ~1–~20 nm in diameter (often called quantum dots) possess short-range structures that are essentially the same as the bulk semiconductors, yet have optical and/or electronic properties which are dramatically different from the bulk [1–7]. The confinement of electrons within a semiconductor nanocrystal results in the shift of the band gap to higher energy with smaller crystalline size. This effect is known as the "*quantum size effect*" [1–7]. In the strong confinement regime, the actual size of the semiconductor particle determines the allowed energy levels and thus the optical and electronic properties of the material. The characterization of the unique properties of nanocrystals can ultimately lead to identifying many potential uses and applications, ranging from catalysis, ceramics, microelectronics, sensors, pigments, and magnetic storage to drug delivery and biomedical applications [1–7]. The applications of nanoparticles are thus expected to enhance many fields of advanced technology particularly in the areas of catalysis, chemical and biological sensors, optoelectronics, drug delivery, and media storage.

Considerable research interest has been focused on the study of bimetallic nanoalloys due to the additional new properties that may arise from the combination of different compositions of metals on the nanoscale [8–17]. The chemical and physical properties of nanoalloys can be tuned by varying the type of metal, composition, degree of chemical ordering, as well as the size and shape of the nanoalloy crystals. At a fundamental level, information on the evolution of the electronic structures of bimetallic nanoparticles as a function of size, composition and shape, and the associated changes in the optical, catalytic and magnetic properties continue to be a major goal of research in nanostructured materials. On a practical level, the unique properties of metallic and bimetallic nanoparticles are exploited for a variety of applications, including nanocatalysis particularly for efficient selective catalysts, sensors, optical markers and filters, fuel and oil additives for energy enhancement and surface modifications as well as many other applications [18–50].

The synthesis and characterization of metallic nanocrystals and bimetallic nanoalloys with controlled size and shape have attracted rapidly growing interest both for fundamental scientific interest and many practical and technological applications [1–50]. A wide range of scientifically interesting and technologically important nanoparticles have been produced by both chemical and physical methods [1–17]. Examples of these approaches include solvothermal methods, template-assisted, kinetic growth control, sonochemical reactions, thermolysis of single-source precursor in ligating solvents, and microwave irradiation (MWI) methods [51–68]. The synthesis of nanocrystals by colloidal methods involves nucleation (the initial formation of the appropriate semiconductor bond), growth (the formation of a highly crystalline core) and passivation of the nanocrystal surface [7,56,69]. The passivation step is important in stabilizing the colloid and controlling the growth of the nanoparticles, preventing the agglomeration and fusing of the particles, and allowing the solubility of the nanoparticles in common solvents [7,56,69].

In this chapter, we describe several chemical methods for the synthesis of nanoalloys with more focus on the MWI methods [59–68]. The MWI approach provides simple and fast routes to the synthesis of nanomaterials since no high temperature or high pressure is needed. Furthermore, MWI is particularly useful for a controlled large-scale synthesis that minimizes the thermal gradient effects [59–68,70–78]. The heating of a substance by MWI depends on the ability of the material (solvent or reagent) to absorb microwave radiation and convert it into heat. This is based on two principal mechanisms: dipole rotation and ionic conduction, that is, by reversal of solvent dipoles and the resulting replacement of charged ions of a solute [79,80]. Polar reactants with a high microwave extinction coefficient can be excited by direct absorption of microwaves. Due to the difference in the solvent and reactant dielectric constants, selective dielectric heating can provide significant enhancement in reaction rates. By using metal precursors that have large microwave absorption cross-sections relative to the solvent, very high effective reaction temperatures can be achieved. The rapid transfer of energy directly to the reactants (faster than they are able to relax) causes an instantaneous internal temperature rise. Thus, the activation energy is essentially decreased as compared with conductive heating and the reaction rate increases accordingly. As a consequence, reactions might be performed at lower temperatures and hotspots or other temperature inhomogeneities can be prevented. Furthermore, reaction parameters such as temperature, time, and pressure can be controlled easily. This also allows the rapid decomposition of the precursors thus creating highly supersaturated solutions where nucleation and growth can take place to produce the desired nanocrystalline products. These conditions lead to the formation of very small nanocrystals since the higher the supersaturation the smaller the critical size required for nucleation. For the formation of nanoalloys, the experimental conditions must be chosen to yield binary nucleation events where the initial nuclei contain both metals with compositions that reflect the compositions of the two metal precursors. This requires careful choice of the two metal precursors with almost identical decomposition profiles to ensure the occurrence of binary nucleation events. These conditions are different from those involved in the formation of core–shell nanoparticles, where the shell atoms heterogeneously nucleate on the preexisting core nuclei. Following the nucleation events, the growth of the nanoalloy nanocrystals can be effectively inhibited by the adsorption of ligating organic surfactants that bind strongly to the nanocrystals, thus stabilizing and passivating the surface. In nanoalloys, depending on the surface composition of the binary nanocrystal faces, selective adsorption of the capping agents can result in controlling the final shape of the grown nanocrystal. Since in MWI it is possible to quench the reaction very early on ($\sim$10 s), this provides the opportunity of controlling the nanostructures from small spherical nuclei to short rods to extended assemblies of nanowires by varying the MWI reaction time, the composition of the nanoalloy, and the type and concentration of different capping agents that exhibit variable binding strengths to the metals in the nanocrystal [70–78].

The organization of the chapter is as follows. First, we present a brief overview of the classical nucleation theory (CNT) since nucleation and growth greatly influence

the control of the size and shape of nanoparticles which consequently determine the unique properties that may characterize nanoparticles [80–84]. Second, we describe conventional chemical methods for the synthesis of nanalloys using reduction and precipitation of mixed-metal hydroxide solutions and chemical reduction of mixed metal cations. Third, we present detailed description of the MWI method as a general procedure for the synthesis of a variety of high quality, crystalline bimetallic nanoalloys with controlled size and shape. The synthesis and characterization of several bimetallic alloys of Au, Pt and Pd with Ru, Rh, Ag, Cu, and Ni will be presented. Finally, we discuss the application of bimetallic nanocrystals in the area of nanocatalysis and describe the synthesis of selected nanoalloys supported on ceria nanoparticles as nanocatalysts for CO oxidation. This demonstrates another advantage of using the MWI approach where a supported nanoalloy catalyst can be prepared using a facile one-pot synthesis.

1.2 Brief overview of nucleation and growth from the vapor phase

Nucleation of liquid droplets from the vapor phase can occur homogeneously or heterogeneously. Homogeneous nucleation occurs in the absence of any foreign particles or surfaces when the vapor molecules themselves cluster to nuclei within the supersaturated vapor. According to the CNT, embryonic clusters of the new phase can be described as spherical liquid droplets with the bulk liquid density inside and the vapor density outside [81,82]. The free energy of these clusters relative to the vapor is the sum of two terms: a positive contribution from the surface free energy and a negative contribution from the bulk free-energy difference between the supersaturated vapor and the liquid. The surface free energy results from the reversible work used in forming the interface between the liquid droplet and the vapor. For a cluster containing n atoms or molecules, the interface energy is given by

$$\sigma A(n) = 4\pi\sigma(3v/4\pi)^{2/3}n^{2/3} \tag{1.1}$$

where σ is the interfacial tension or surface energy per unit area, $A(n)$ is the surface area of the clusters, and v is the volume per molecule in the bulk liquid. Since n molecules are transferred from the vapor to the liquid, the bulk contribution to the free energy is $n(\mu_\ell - \mu_v)$ where μ_ℓ. and μ_v are the chemical potentials per molecule in the bulk liquid and vapor, respectively. Assuming *ideal* vapor, it can be shown that

$$(\mu_\ell - \mu_v) = -n\mathrm{k_B}T \ln S \tag{1.2}$$

where $\mathrm{k_B}$ is the Boltzmann constant, T is the temperature, and S is vapor supersaturation ratio defined as $S = P/P_e$, where P is the pressure of the vapor and P_e is the equilibrium or "saturation" vapor pressure at the temperature of the vapor T.