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Nanocrystals: Synthesis, Properties and Applications

纳米晶体
——合成、性质和应用
(影印版)

[印] 拉奥(C. N. R. Rao)
[印] 托马斯(P. J. Thomas) 著
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序 言

物理学是研究物质、能量以及它们之间相互作用的科学。她不仅是化学、生命、材料、信息、能源和环境等相关学科的基础,同时还是许多新兴学科和交叉学科的前沿。在科技发展日新月异和国际竞争日趋激烈的今天,物理学不仅囿于基础科学和技术应用研究的范畴,而且在社会发展与人类进步的历史进程中发挥着越来越关键的作用。

我们欣喜地看到,改革开放三十多年来,随着中国政治、经济、教育、文化等领域各项事业的持续稳定发展,我国物理学取得了跨越式的进步,做出了很多为世界瞩目的研究成果。今日的中国物理正在经历一个历史上少有的黄金时代。

在我国物理学科快速发展的背景下,近年来物理学相关书籍也呈现百花齐放的良好态势,在知识传承、学术交流、人才培养等方面发挥着无可替代的作用。从另一方面看,尽管国内各出版社相继推出了一些质量很高的物理教材和图书,但系统总结物理学各门类知识和发展,深入浅出地介绍其与现代科学技术之间的渊源,并针对不同层次的读者提供有价值的教材和研究参考,仍是我国科学传播与出版界面临的一个极富挑战性的课题。

为有力推动我国物理学研究、加快相关学科的建设与发展,特别是展现近年来中国物理学家的研究水平和成果,北京大学出版社在国家出版基金的支持下推出了《中外物理学精品书系》,试图对以上难题进行大胆的尝试和探索。该书系编委会集结了数十位来自内地和香港顶尖高校及科研院所的知名专家学者。他们都是目前该领域十分活跃的专家,确保了整套丛书的权威性和前瞻性。

这套书系内容丰富,涵盖面广,可读性强,其中既有对我国传统物理学发展的梳理和总结,也有对正在蓬勃发展的物理学前沿的全面展示;既引进和介绍了世界物理学研究的发展动态,也面向国际主流领域传播中国物理的优秀专著。可以说,《中外物理学精品书系》力图完整呈现近现代世界和中国物理

科学发展的全貌,是一部目前国内为数不多的兼具学术价值和阅读乐趣的经典物理丛书。

《中外物理学精品书系》另一个突出特点是,在把西方物理的精华要义“请进来”的同时,也将我国近现代物理的优秀成果“送出去”。物理学科在世界范围内的重要性不言而喻,引进和翻译世界物理的经典著作和前沿动态,可以满足当前国内物理教学和科研工作的迫切需求。另一方面,改革开放几十年来,我国的物理学研究取得了长足发展,一大批具有较高学术价值的著作相继问世。这套丛书首次将一些中国物理学者的优秀论著以英文版的形式直接推向国际相关研究的主流领域,使世界对中国物理学的过去和现状有更多的深入了解,不仅充分展示出中国物理学研究和积累的“硬实力”,也向世界主动传播我国科技文化领域不断创新的“软实力”,对全面提升中国科学、教育和文化领域的国际形象起到重要的促进作用。

值得一提的是,《中外物理学精品书系》还对中国近现代物理学科的经典著作进行了全面收录。20世纪以来,中国物理界诞生了很多经典作品,但当时大都分散出版,如今很多代表性的作品已经淹没在浩瀚的图书海洋中,读者们对这些论著也都是“只闻其声,未见其真”。该书系的编者们在这方面下了很大工夫,对中国物理学科不同时期、不同分支的经典著作进行了系统的整理和收录。这项工作具有非常重要的学术意义和社会价值,不仅可以很好地保护和传承我国物理学的经典文献,充分发挥其应有的传世育人的作用,更能使广大物理学人和青年学子亲身体会我国物理学研究的发展脉络和优良传统,真正领悟到老一辈科学家严谨求实、追求卓越、博大精深的治学之美。

温家宝总理在2006年中国科学技术大会上指出,“加强基础研究是提升国家创新能力、积累智力资本的重要途径,是我国跻身世界科技强国的必要条件”。中国的发展在于创新,而基础研究正是一切创新的根本和源泉。我相信,这套《中外物理学精品书系》的出版,不仅可以使所有热爱和研究物理学的人们从中获取思维的启迪、智力的挑战和阅读的乐趣,也将进一步推动其他相关基础科学更好更快地发展,为我国今后的科技创新和社会进步做出应有的贡献。

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2010年5月于燕园

C.N.R. Rao P.J. Thomas G.U. Kulkarni

Nanocrystals: Synthesis, Properties and Applications

With 113 Figures, 6 in Color and 5 Tables

Preface

Nanoscience has emerged to become one of the most exciting areas of research today and has attracted the imagination of a large body of students, scientists, and engineers. The various kinds of nanomaterials that one normally deals with are the zero-dimensional nanocrystals, one-dimensional nanowires and nanotubes, and two-dimensional nanofilms and nanowalls. Of these, one of the earliest research investigations pertains to nanocrystals. It is truly remarkable that Michael Faraday made nanocrystals of gold and other metals in solution way back in 1857. Nanocrystals occupy a special place amongst nanomaterials because they have enabled a proper study of size-dependent properties. There have been several reviews, books, and conference proceedings dealing with nanomaterials in the last few years. In this monograph, we have attempted to give a well-rounded presentation of various aspects of nanocrystals. We first discuss some of the fundamentals and then make a detailed presentation of the synthetic methods. We examine the process of assembly of nanocrystals as well as their properties. Core-shell nanoparticles are treated as a separate chapter, just as the applications of the nanocrystals. We believe that this monograph should be useful to practicing scientists, research workers, teachers, and students all over the world. It could also form the basis of a course on the subject.

Bangalore
January 2007

C.N.R. Rao
P.J. Thomas
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Basics of Nanocrystals

1.1 Introduction

Nanoparticles constitute a major class of nanomaterials. Nanoparticles are zero-dimensional, possessing nanometric dimensions in all the three dimensions. The diameters of nanoparticles can vary anywhere between one and a few hundreds of nanometers. Small nanoparticles with diameters of a few nanometers are comparable to molecules. Accordingly, the electronic and atomic structures of such small nanoparticles have unusual features, markedly different from those of the bulk materials. Large nanoparticles ($>20\text{--}50\text{ nm}$), on the other hand, would have properties similar to those of the bulk [1]. The change in a material property as a function of size is shown schematically in Fig. 1.1. At small sizes, the properties vary irregularly and are specific to each size. At larger sizes, dependence on size is smooth and scaling laws can be derived to describe the variation in this regime. The size-dependent properties of nanoparticles include electronic, optical, magnetic, and chemical characteristics. Nanoparticles can be amorphous or crystalline. Being small in size, crystalline nanoparticles can be of single domain. Nanoparticles of metals, chalcogenides, nitrides, and oxides are often single crystalline. Crystalline nanoparticles are referred to as nanocrystals.

Nanoparticles are not new and their history can be traced back to the Roman period. Colloidal metals were used to dye glass articles and fabrics and as a therapeutic aid in the treatment of arthritis. The Purple of Cassius, formed on reacting stannic acid with chloroauric acid, was a popular purple dye in the olden days. It is actually made up of tin oxide and Au nanocrystals [2]. The Romans were adept at impregnating glass with metal particles to achieve dramatic color effects. The Lycurgus cup, a glass cup of 4th century AD, appears red in transmitted light and green in reflected light. This effect, which can be seen in the cup preserved in the British museum in London, is due to Au and Ag nanocrystals present in the walls of the cup. Maya blue, a blue dye employed by the Mayas around 7th century AD has been shown recently to consist of metal and oxide nanocrystals in addition to indigo and silica [3].

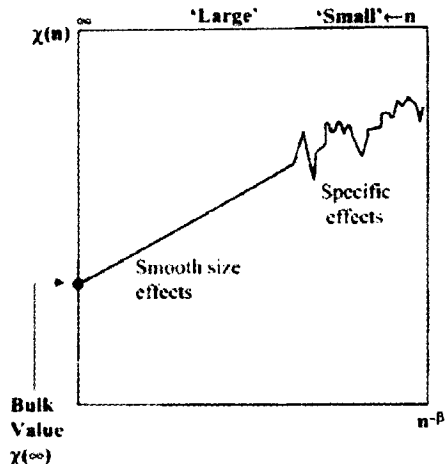


Fig. 1.1. The size dependence of a property $\chi(n)$ on the number of atoms (n) in a nanoparticle. The data are plotted against $n^{-\beta}$ where $\beta \geq 0$. Small nanoparticles reveal specific size effects, while larger particles are expected to exhibit a smooth size dependence, converging to the bulk value (reproduced with permission from [1])

Clearly, the ability to synthesize nanoparticles preceded the understanding of nanoscale phenomena. Systematic studies of nanoparticles began to appear as early as the seventeenth century. Antonio Neri, a Florentine glass maker and priest, describes the synthesis of colloidal gold in his 1612 treatise *L'Arte Vetraria*. John Kunckel, revised and translated Neri's work into German in 1689. Kunckel is often credited with the discovery that glass can be colored red by addition of gold.

Despite the early advances, studies of nanoscale particles did not gather momentum in later years. Thus, for most part of the 20th century, colloid science was the domain of a few specialized groups and did not receive sufficient importance. As early as 1857, Michael Faraday [4] carried out ground-breaking work on colloidal metals. He called them divided metals. Faraday established the very basis for the area, noting that colloidal metal sols were thermodynamically unstable, and that the individual particles must be stabilized kinetically against aggregation. Note that sols are dispersions of solids in liquids. Once the particles in a sol coagulate, the process cannot be reversed. Remarkably, Faraday also identified the essence of the nature of colloidal, nanoscale particles of metals. In the case of gold, he stated "gold is reduced in exceedingly fine particles which becoming diffused, produce a beautiful fluid . . . the various preparations of gold whether ruby, green, violet, or blue . . . consist of that substance in a metallic divided state." Einstein [5] related the Brownian motion executed by the nanoparticles to their diffusion coefficient. Mie and Gans [6–8] proposed a theoretical basis for the optical properties of the nanoscale particles, which continues to be used widely to this day. Frölich and Kubo proposed

theories that predicted that the electronic structure of colloidal metals would differ from bulk.

The neglect of colloid science prompted Ostwald [9] to title his 1915 book on colloids as "The world of neglected dimensions." This period also witnessed advances in methods to make colloidal gold. Bredig [10] prepared Au sols by striking an arc between Au electrodes immersed in dilute alkali. Donau [11] suggested that passing CO through a solution of chloroauric acid provided a gold sol. Zsigmondy [12] discovered the seeding method and was familiar with the use of formaldehyde in mild alkali to produce Au sols from salts. The 1925 award of the Nobel prize to Zsigmondy partly for his work on gold colloids did not seem to have enthused the scientific community to pursue this area of research. In the last few years, however, there has been a great upsurge in the use of colloid chemical methods to generate nanoparticles of various materials. This is because of the excitement caused by the science of nanomaterials initiated by the now famous lecture of Feynman [13].

Explosion of research in nanocrystals has been so dramatic that very few of the modern practitioners seem to be aware of the glorious past of colloid science. The progress has been facilitated in part by the advances in instrumentation that have helped in fully characterizing nanomaterials. Today, it is possible to prepare and study nanocrystals of metals, semiconductors and other substances by various means. Advances in both experimental and theoretical methods have led to an understanding of the properties of nanocrystals.

1.2 Properties of Nanocrystals

Nanocrystals of materials are generally obtainable as sols. Sols containing nanocrystals behave like the classical colloids. For example, the stability of a dispersion depends on the ionic strength of the medium. Nanocrystalline sols possess exceptional optical clarity. A key factor that lends stability to nanocrystal sols is the presence of a ligand shell, a layer of molecular species adsorbed on the surface of the particles. Without the ligand shell, the particles tend to aggregate to form bulk species that flocculate or settle down in the medium. Depending on the dispersion medium, the ligands lend stability to particles in two different ways. Thus, in an aqueous medium, coulomb interactions between charged ligand species provide a repulsive force to counter the attractive van der Waals force between the tiny grains, by forming an electrical double layer. In an organic medium, the loss of conformational freedom of the ligands and the apparent increase in solute concentration provide the necessary repulsive force. We illustrate this schematically in Fig. 1.2. Nanocrystals dispersed in liquids are either charge-stabilized or sterically stabilized.

Nanoparticles devoid of ligands are generally studied in vacuum. Such particles deposited on a substrate are readily examined by photoelectron spectroscopy and other techniques. Beams of uniformly sized clusters traversing

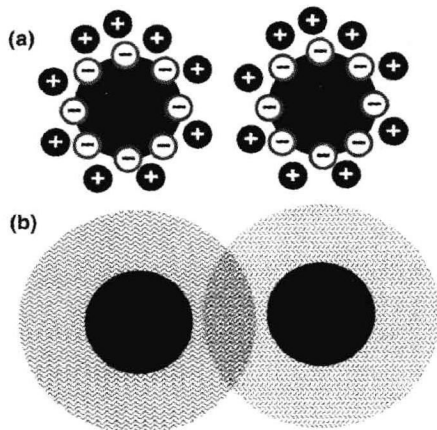


Fig. 1.2. Schematic illustration of the factors lending stability to a colloidal dispersion: (a) an electric double layer and (b) loss of conformational freedom of chain-like ligands

a vacuum chamber (cluster beams) with some fixed velocity provide opportunities for studies of the intrinsic physical properties of nanoparticulate matter.

1.2.1 Geometric Structure

The dimensions of nanocrystals are so close to atomic dimensions that an unusually high fraction of the total atoms would be present on their surfaces. For example, a particle consisting of 13 atoms, would have 12 atoms on the surface, regardless of the packing scheme followed. Such a particle has a surface more populated than the bulk. It is possible to estimate the fraction of atoms on the surface of the particle (P_s , percentage) using the simple relation,

$$P_s = 4N^{-1/3} \times 100, \quad (1.1)$$

where N is the total number of atoms in the particle [14]. The variation of the surface fraction of atoms with the number of atoms is shown in Fig. 1.3. We see that the fraction of surface atoms becomes less than 1% only when the total number of atoms is of the order of 10^7 , which for a typical metal would correspond to a particle diameter of 150 nm.

Nanoparticles are generally assumed to be spherical. However, an interesting interplay exists between the morphology and the packing arrangement, specially in small nanocrystals. If one were to assume that the nanocrystals strictly follow the bulk crystalline order, the most stable structure is arrived at by simply constraining the number of surface atoms. It is reasonable to assume that the overall polyhedral shape has some of the symmetry elements of the constituent lattice. Polyhedra such as the tetrahedron, the octahedron,

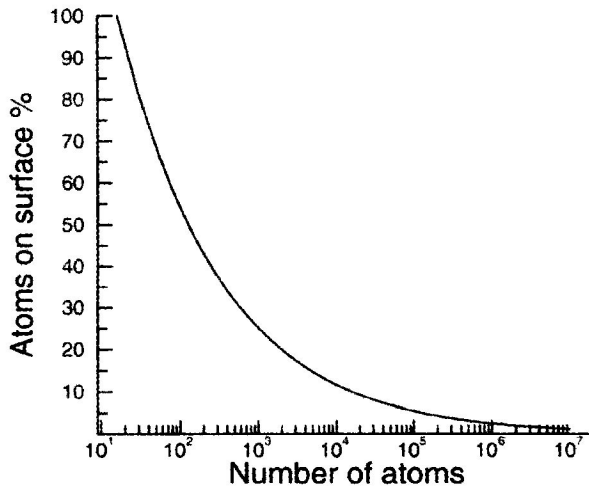


Fig. 1.3. Plot of the number of atoms vs. the percentage of atoms located on the surface of a particle. The calculation of the percentage of atoms is made on the basis of (1.1) and is valid for metal particles

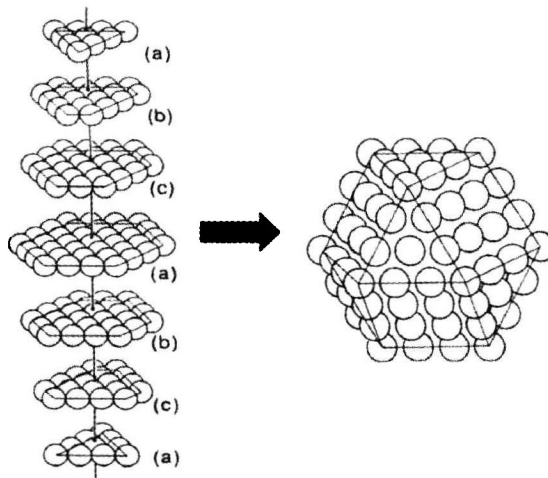


Fig. 1.4. Schematic illustration of how a cuboctahedral 147 atom-cluster, composed of seven close-packed layers can be made out of a stacking sequence reminiscent of a fcc lattice (reproduced with permission from [16])

and the cuboctahedron can be constructed following the packing scheme of a fcc lattice [15, 16]. Figure 1.4 shows how a cuboctahedral cluster of 146 constituent atoms follows from a fcc type *abcabc* layer stacking. In contrast to the above, small clusters frequently adopt *non-close packed* icosahedral

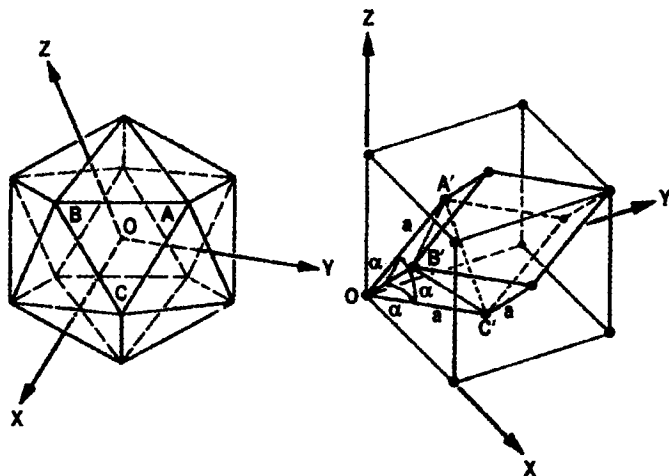


Fig. 1.5. The regular icosahedron is made up of twenty irregular tetrahedra like OABX. The rhombohedral cell in a fcc lattice ($OA'B'C'$) has $\alpha = 60^\circ$. When α is distorted to 63.43° , $OA'B'C'$ and OABC become similar. Small nanocrystals distort in a similar manner from regular fcc lattice to adopt the icosahedral shape

or dodecahedral shapes. The clusters adopting such schemes suffer a loss in packing efficiency. The icosahedron has a fivefold symmetry, inconsistent with the packing requirements of a regular crystalline lattice with long-range order. While employing close packing schemes, a stacking fault becomes necessary to arrive at an icosahedral arrangement. Such a scheme is outlined in Fig. 1.5.

The icosahedron which has twenty triangular faces and twelve vertices consists of a fcc-like close packing. Each of the twenty triangular faces of an icosahedron can be considered as a base of a tetrahedron, whose apex is at the inversion center (see Fig. 1.5a). A tetrahedron $OA'B'C'$ in Fig. 1.5b joining three face-centered atoms and an atom at the base of a fcc unit cell has the angle, $\alpha = 60^\circ$. These angles can be distorted to 63.43° , to obtain the tetrahedron (OABC) that forms the building block of an icosahedron. Such a distortion results in the lowering of the packing fraction from 0.74080 to 0.68818. Several theoretical investigations have sought to explain the unusual stability of icosahedral clusters [17–19]. Allpress and Sanders [20, 21], based on potential energy calculations, showed that the binding energy per atom is lower than that in a corresponding octahedron containing the same number of atoms. Molecular dynamics simulations have shown that Al clusters with nuclearities upto 147 atoms exhibit distorted icosahedral structures while Al_{147} has a cuboctahedral shape [22]. More rigorous theories (ab initio, density functional) broadly support this contention. A decahedral shape can be thought of as being made up of four edge-sharing tetrahedra, followed by some relaxation and the consequent loss of packing fraction. Ino [23, 24]

has suggested the use of the term “multiply twinned particle” to denote a decahedral particle, and such particles obtained by the twinning of tetrahedra.

The properties of nanocrystals are also influenced by the formation of geometric shells which occur at definite nuclearities [25, 26]. Such nuclearities, called magic nuclearities endow a special stability to nanocrystals as can be demonstrated on the basis of purely geometric arguments. A new shell of a particle emerges when the coordination sphere of an inner central atom or shell (forming the previous shell) is completely satisfied. The number of atoms or spheres required to complete successive coordination shells is a problem that mathematicians, starting with Kepler, have grappled with for a long time [27, 28]. The “kissing” problem, as it is known in the mathematical world, was the subject of a famous argument between Newton and Gregory at Cambridge. In retrospect, Newton, who held that 12 atoms are required to complete the second shell was indeed correct. An idea of the mathematical effort involved can be gauged from the fact that the proof of Newton’s argument was provided only in 2002. It is quite apparent that the ultimate shape of the emerging crystallite should play a role in determining the number of atoms that go into forming complete shells. The magic nuclearities would then yield information on the morphology of the cluster. By a strange coincidence, the number of atoms required to form complete shells in the two most common shapes (icosahedron and cuboctahedron) is the same.

The number of atoms, N , required to form a cluster with L geometric shells is given by

$$N = \frac{(10L^3 + 15L^2 + 11L + 3)}{3}. \quad (1.2)$$

This represents the solution for the “kissing” problem in three dimensions and is valid for icosahedral and cuboctahedral morphologies. For other shapes, the reader may refer to a paper from the group of Martin [29]. Particles possessing the above number of atoms are said to be in a closed-shell configuration. The number of atoms required to fill up coordination shell completely, n_L of a particular shell, is given by

$$n_L = (10n_{L-1}^2 + 2). \quad (1.3)$$

where $n_0=1$. Thus, 12 atoms are required to complete the first shell, 42 to complete the second shell etc. A schematic illustration of the observed magic nuclearity clusters is provided in Fig. 1.6. The notion of the closed-shell configuration can be extended to larger dimensions as well. Closed-shell configurations lend stability to giant clusters made of clusters and even to a cluster of giant clusters.

Determination of the structures of nanocrystals should ideally follow from X-ray diffraction, but small particles do not diffract well owing to their limited size. The peaks in the diffraction pattern are less intense and are broad. Structural studies are therefore based on high resolution transmission electron microscopy (HRTEM), extended X-ray absorption fine structure (EXAFS),