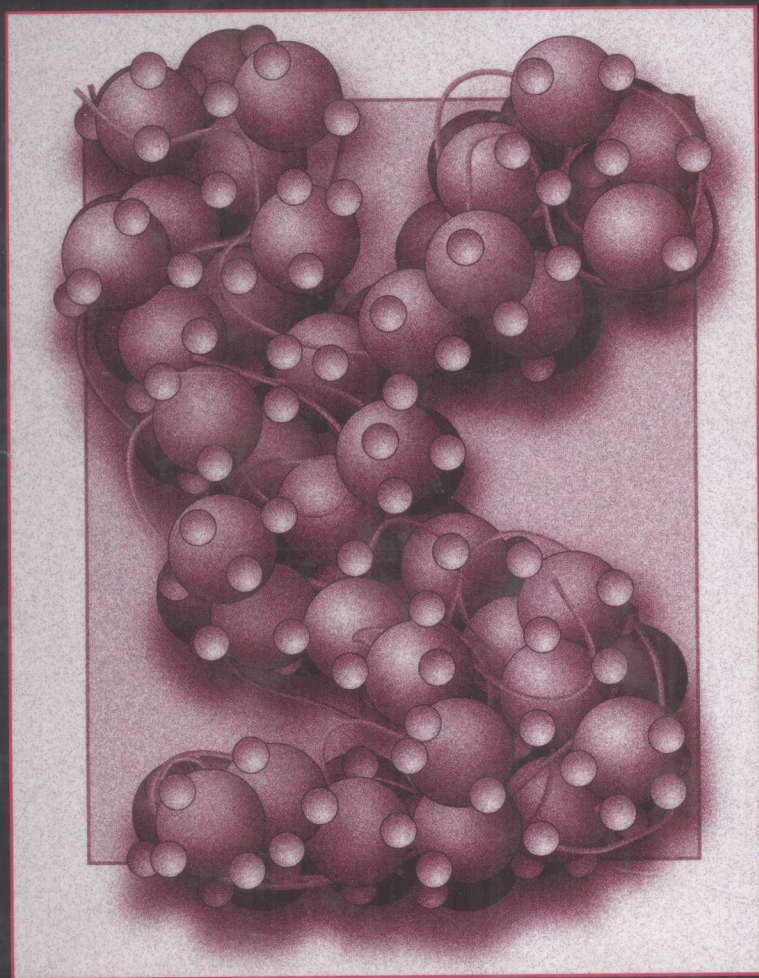


NANOSTRUCTURE SCIENCE AND TECHNOLOGY
Series Editor: David J. Lockwood

Nanoparticles

Building Blocks for Nanotechnology



Edited by
Vincent Rotello

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Building Blocks for Nanotechnology

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Nanoparticles

Building Blocks for Nanotechnology

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Preface

The integration of top-down lithographic techniques with synthetic organic and inorganic technologies is a key challenge for the development of effective nanoscale devices. In terms of assembly, nanoparticles provide an excellent tool for bridging the gap between the resolution of electron beam lithography (~60 nm) and the molecular level. Nanoparticles possess an array of unique properties associated with their core materials, including distinctive magnetic, photonic and electronic behavior. This behavior can be controlled and applied through monolayer functionalization and assembly strategies, making nanoparticles both scaffolds and building blocks for nanotechnology.

The diverse structures and properties of nanoparticles makes them useful tools for both fundamental studies and pragmatic applications in a range of disciplines. This volume is intended to provide an integrated overview of the synthesis and assembly of nanoparticles, and their applications in chemistry, biology, and materials science.

The first three chapters focus on the creation and intrinsic properties of nanoparticles, covering some of the myriad core materials and shapes that have been created. The remaining chapters of the book discuss the assembly of nanoparticles, and applications of both discrete particles and particle assemblies in a wide range of fields, including device and sensor fabrication, catalysis, biology, and nanoscale electronic and magnetic systems.

Of course, no single book can hope to cover the diverse array of research encompassed by researchers making and applying nanoparticles. I hope, however, that this book will prove useful for whetting the imagination of researchers currently pursuing nanotechnology, as well as those contemplating joining this uniquely multidisciplinary field.

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1

Synthesis and Applications of Magnetic Nanoparticles

Andrew K. Boal

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1.1. INTRODUCTION

Magnetic nanoparticles (MNPs) have been the focus of an increasing amount of the recent literature, which has chronicled research into both the fabrication and applications of MNPs. The explosion of research in this area is driven by the extensive technological applications of MNPs which includes single-bit elements in high-density magnetic data storage arrays, magneto-optical switches, and novel photoluminescent materials. In biomedicine, MNPs serve as contrast enhancement agents for Magnetic Resonance Imaging, selective probes for bimolecular interactions, and cell sorters. Nanoparticles of magnetic metals are also finding applications as catalysts, nucleators for the growth of high-aspect-ratio nanomaterials, and toxic waste remediation. Methodologies for the synthesis of MNPs are being developed by scientists working in fields spanning Biology, Chemistry, and Materials Science. In the last decade, these efforts have provided access to nanoscale magnetic materials ranging from inorganic metal clusters to custom-built Single Molecule Magnets. The goal of this chapter is to provide broad overviews of both the applications of MNPs and the synthetic methodologies used in their production.^{1,2}

1.2. APPLICATIONS OF MAGNETIC NANOPARTICLES

High-density magnetic data storage arrays provide a major technological driving force for the exploration of MNPs. If a reliable data storage system based on a single 5 nm MNP acting as an individual bit of information could be created, storage densities of 10 Gbit/cm² would be possible.³ MNPs have also been demonstrated to be functional elements in magneto-optical switches,⁴ sensors based on Giant Magnetoresistance,⁵ and magnetically controllable Single Electron Transistor devices⁶ or photonic crystals.⁷ One of the first stages in the development these MNP-based materials is the creation of ordered 2- and 3-dimensional arrays of MNPs.⁸ Two dimensional arrays are typically fabricated by the slow evaporation of highly monodisperse MNP solutions onto a substrate.⁹ Structural control can be achieved by the application of a magnetic field¹⁰ or patterning using dip-pen nanolithography.¹¹ Three dimensional nanoparticle assemblies with complex structures can also be fabricated by the slow evaporation technique in the presence of an applied magnetic field.¹² These technological applications are all in addition to the numerous known and developed applications of aqueous suspensions of MNPs (ferrofluids).¹³

Doping magnetic ions into semiconductors to produce Dilute Magnetic Semiconductors (DMS) has long been used to alter the electronic and optical properties of the parent materials.¹⁴ Similarly, DMS nanoparticles can be produced by including metal ions in reactions used to prepare semiconductor nanoparticles.¹⁵ DMS nanoparticles have applications in the fabrication of novel optical materials. For example, both Ni:ZnS and Co:ZnS DMS nanoparticles display strong photoluminescent emission of green light.¹⁶ Additionally, the electronic properties of DMS materials are responsive to both light and magnetic fields, making them useful in the fabrication of magneto-optical switches.¹⁷

MNPs are also finding a multitude of biomedical applications, the most prevalent of which is Magnetic Resonance Imaging (MRI) contrast agents.¹⁸ Recent work has involved the development of bioconjugated MNPs,¹⁹ which facilitate specific targeting of these MRI probes to brain tumors²⁰ and enabled real-time monitoring of both gene expression²¹ and T-cell²² or progenitor cell²³ migration. Bioconjugate MNPs are also useful as probes for *in vitro* detection of bimolecular interactions using a variety of techniques, including the detection of DNA hybridization by NMR.²⁴ Antigen-antibody interactions can be detected using either Superconducting Quantum Interference Device (SQUID)²⁵ or magnetically induced birefringence²⁶ based immunoassays. MNPs have also been utilized in the purification of both cells²⁷ and biomacromolecules²⁸ from complex mixtures. In purification applications, the MNP is modified so as to specifically bind the target cell or molecule of interest and the complex is then magnetically purified from undesired components.

MNPs are also used as highly active catalysts which has long been demonstrated by the use of finely divided metals in several reactions.²⁹ Recent synthetic advances have resulted in the preparation of catalysts based on smaller particles or matrix supported nanoparticle catalysts. Smaller particles increase the

surface-to-area ratio and therefore the catalytic activity while supported nanoparticle catalyst materials show enhanced stability and broader scope of applications.³⁰ Electro-oxidation of methanol for fuel cells applications can be catalyzed by NiPt, PtRuNi,³¹ and CoPt³² nanoparticles. Similarly, LiCoO₂³³ and Li_xCu_{1-y}Fe_yO_z³⁴ nanoparticles have been evaluated as potential components of lithium-ion batteries. Finally, recent reports have described the application of Co nanoparticles in the Pauson-Khand reaction.³⁵

MNPs can nucleate and control the growth of high aspect ratio nanomaterials such as carbon nanotubes (CNTs). Here, a substrate is coated with nanoparticles and CNTs are then grown using a variety of chemical vapor deposition (CVD) processes. Nanoparticles of Fe, Ni, Co,³⁶ FeMo,³⁷ and iron carbides³⁸ have all been shown to be active in this process. In the case of Fe nanoparticles, the diameter of the nucleating nanoparticle has been shown to control the diameter of the resulting CNT over the range of 3-13 nm.³⁹ Iron nanoparticles have also been used to nucleate the growth of iron nanorods.⁴⁰

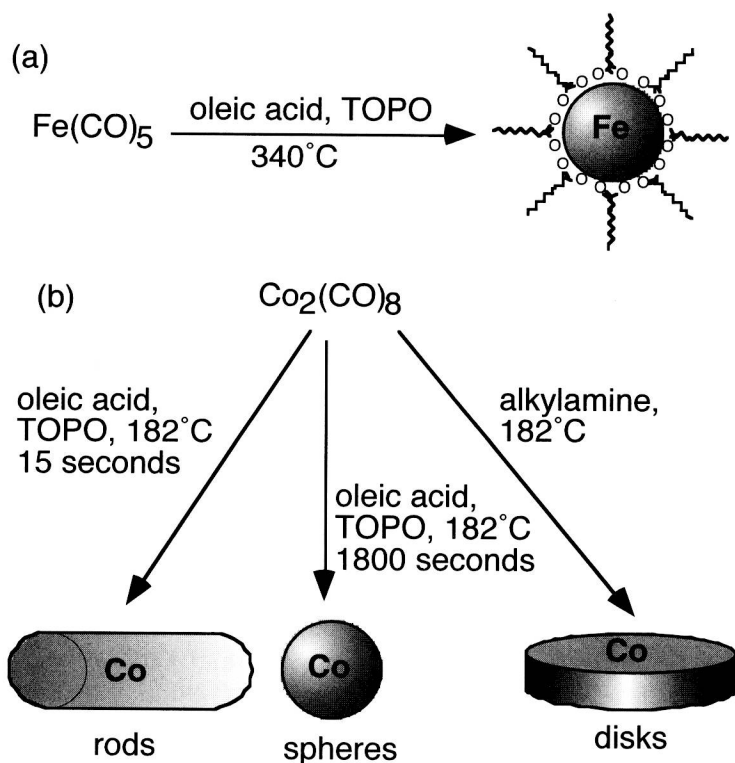
Finally, iron nanoparticles have also been used as toxic waste remediators. Bulk iron is an established waste remediator as, in aqueous solutions, it acts as a reducing agent capable of decomposing a variety of toxic chemicals in groundwater including halogenated alkanes⁴¹ and nitroaromatics.⁴² Owing to their higher surface-to-area ratio, nanoparticles are more efficient at waste remediation, as demonstrated for FePd nanoparticles used to decompose halogenated alkanes⁴³ and Fe nanoparticles acting to remove Cr⁴⁺ and Pb²⁺ from aqueous solutions.⁴⁴

1.3. SYNTHESIS OF SINGLE METAL MNPS

Solution phase synthesis of transition metal nanoparticles is accomplished via two generic pathways: the reduction of a metal salt or decomposition of an organometallic complex. Two of the largest concerns regarding MNP synthesis are the ability to both tune the size of the nanoparticle and control particle size dispersity. These concerns are addressed in a number of ways and are dependent on the synthetic methodology employed. In the case of metal ion reduction, successful strategies include conducting the reaction in a confined environment or in the presence of a suitable capping ligand. For the case of organometallic decomposition, size control and dispersity is usually attained by conducting the reactions at high temperature, which ensures a high rate of nanoparticle nucleation and growth. Capping ligands, which form a self-assembled monolayer of the nanoparticle, can also be used to mediate particle growth.

Water-in-oil microemulsions (w/o microemulsions) and inverse micelles are often employed as nanoconfined reactors in the synthesis of many varieties of nanoparticles.⁴⁵ For both, the size of the confined space can be defined by varying the amounts of both surfactant and solvent, which allows for direct control over the size of the resulting MNPs. Typically, MNP preparation in w/o

tetraethylenepentamine.⁵¹ Thermal decomposition of $\text{Co}_2(\text{CO})_8$ in hot toluene solutions containing TOPO produces ϵ -Co MNPs.⁵² Similar reactions carried out in *o*-dichlorobenzene in the presence of various ligands allows for MNP morphological control (Scheme 1.2b).⁵³ Co MNPs embedded in polymers have been prepared both by H_2 promoted decomposition of $\text{Co}(\eta^3\text{-C}_8\text{H}_{13})(\text{COD})$ in poly(vinylpyrrolidone) (PVP)⁵⁴ or by charging either crosslinked poly(styrene)⁵⁵ or poly(dimethylsiloxane)-*block*-poly((3-cyannopropyl)methylsiloxane)-*block*-poly(dimethylsiloxane)⁵⁶ with $\text{Co}_2(\text{CO})_8$ followed by heating. Ni MNPs can be fabricated by H_2 induced decomposition of $\text{Ni}(\text{COD})_2$. By varying the ligands present in the decomposition reaction, the morphology of the resulting Ni MNPs can be varied.⁵⁷ Ni MNPs can also be prepared in PVP matrices either by the direct decomposition of $\text{Ni}(\text{COD})_2$ at room temperature by PVP⁵⁸ or by H_2 promoted decomposition.⁵⁹



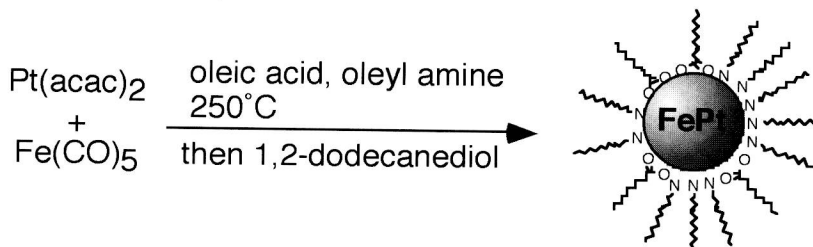
SCHEME 1.2. (a) Thermal decomposition of $\text{Fe}(\text{CO})_5$ in the presence of oleic acid and TOPO to produce Fe MNPs and (b) use of varying ligands to produce Co MNPs with spherical, rod, and disk morphologies from $\text{Co}_2(\text{CO})_8$.

Sonochemical decomposition of organometallic complexes has also been used to produce MNPs. Sonication of $\text{Fe}(\text{CO})_5$ either as a neat liquid or in a noncoordinating, high boiling solvent such as decalin leads to the formation of agglomerates of polydisperse Fe MNPs.⁶⁰ Coordinating ligands or polymers that can attach to the MNP surface prevents agglomeration and allow for better

control over particle size dispersity.⁶¹ Sonication has also be used to produce Ni MNPs by the decomposition of Ni(COD)_2 .⁶²

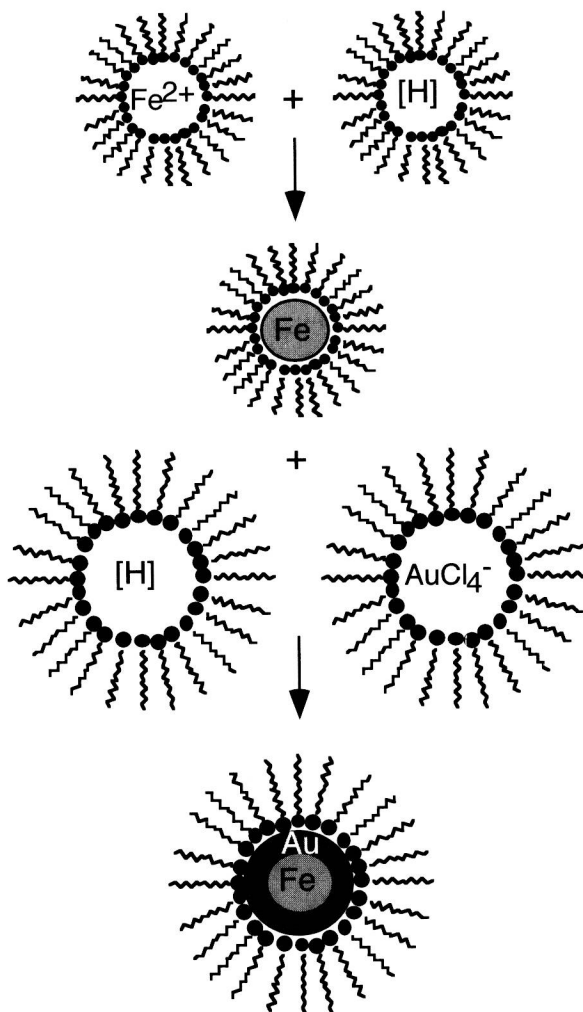
1.4. SYNTHESIS OF ALLOYED METAL NANOPARTICLES

MNPs of alloyed transition metals can be prepared by reactions in which two metal precursors are decomposed in tandem, producing solid solution nanoparticles, or sequentially to give core-shell nanoparticles.⁶³ The most heavily studied alloy MNPs are FePt and CoPt, both of which are of high interest for applications in data storage. FePt MNPs are prepared by the simultaneous thermal decomposition of Fe(CO)_5 to Fe and the polyol reduction of Pt(acac)_2 by 1,2-dodecanediol to Pt at 250°C in solutions containing oleic acid and oleyl amine (Scheme 1.3).⁶⁴ This process yields monodisperse, solid solution FePt MNPs coated by a monolayer of oleyl amine and oleic acid that can be exchanged for shorter or longer acids or amines after synthesis. The composition of the MNP core can be controlled by varying the relative concentrations of the iron and platinum precursors. Further, the diameter of these MNPs can be adjusted between 3-10 nm.



SCHEME 1.3. Synthesis of solid solution FePt MNPs.

Variations on the tandem organometallic decomposition/polyol reduction method allows for the synthesis of MNPs of other alloys of iron. Including either AgAc or Co(acac)_2 in the reaction produces $[\text{Fe}_{49}\text{Pt}_{51}]_{88}\text{Ag}_{12}$ ⁶⁵ or $\text{Fe}_x\text{Co}_y\text{Pt}_{100-x-y}$ ⁶⁶ nanoparticles, respectively. Pd(acac)_2 can be used instead of Pt(acac)_2 to produce MNPs of FePd.⁶⁷ The simultaneous decomposition of Fe(CO)_5 and Mo(CO)_6 in the presence of bis-2-ethylhexylamine and octanoic acid in refluxing dioctyl ether produces FeMo MNPs whose size can be varied between 3-11 nm by changing the amount of acid in the reaction.³⁷ FeAu MNPs can be prepared by reducing w/o micelles of FeSO_4 and HAuCl_4 with NaBH_4 . This procedure has been used to prepare both $\text{Fe}_{\text{core}}\text{Au}_{\text{shell}}$ ⁶⁸ and $\text{Au}_{\text{core}}\text{Fe}_{\text{shell}}\text{Au}_{\text{shell}}$ ⁶⁹ MNPs by a stepwise reduction process where each successive step uses larger diameter water droplets to yield the alloyed particle (Scheme 1.4). Similarly, FeCu nanoparticles can be prepared by the simultaneous reduction of Fe^{2+} and Cu^{2+} in inverse micelles producing MNPs of various FeCu ratios.⁷⁰

SCHEME 1.4. Synthesis of Fe_{core}Au_{shell} MNPs.

CoPt MNPs can be fabricated by several different routes. Simultaneous reaction of $\text{Co}(\eta^3\text{-C}_8\text{H}_{18})(\eta^4\text{-C}_8\text{H}_{12})$ and $\text{Pt}_2(\text{dba})_3$ with H_2 in the presence of PVP leads to the production of 1-1.5 nm diameter, polymer coated MNPs.⁷¹ The composition of these nanoparticles can be varied between Co_3Pt_1 , Co_1Pt_1 , and Co_1Pt_3 by changing the ratio of the inorganic precursors subjected to the reaction. Simultaneous decomposition of $\text{Co}_2(\text{CO})_8$ and reduction of $\text{Pt}(\text{acac})_2$ in the presence of 1-adamantanecarboxylic acid and various coordinating solvents allows for the synthesis of CoPt_3 MNPs with diameters controllable between 1.5-7.2 nm.⁷² Likewise, simultaneous decomposition of $\text{Co}_2(\text{CO})_8$ and either $\text{Rh}(\text{acac})(\text{COD})$ or $\text{Sm}(\text{acac})_3$ in hot surfactants produces solid solution RhCo ⁷³ or SmCo ⁷⁴ MNPs. The simultaneous reduction of PtCl_6^{2-} and Co^{2+} ions by hydrazine in w/o microemulsions leads to the formation of 3-4 nm diameter CoPt