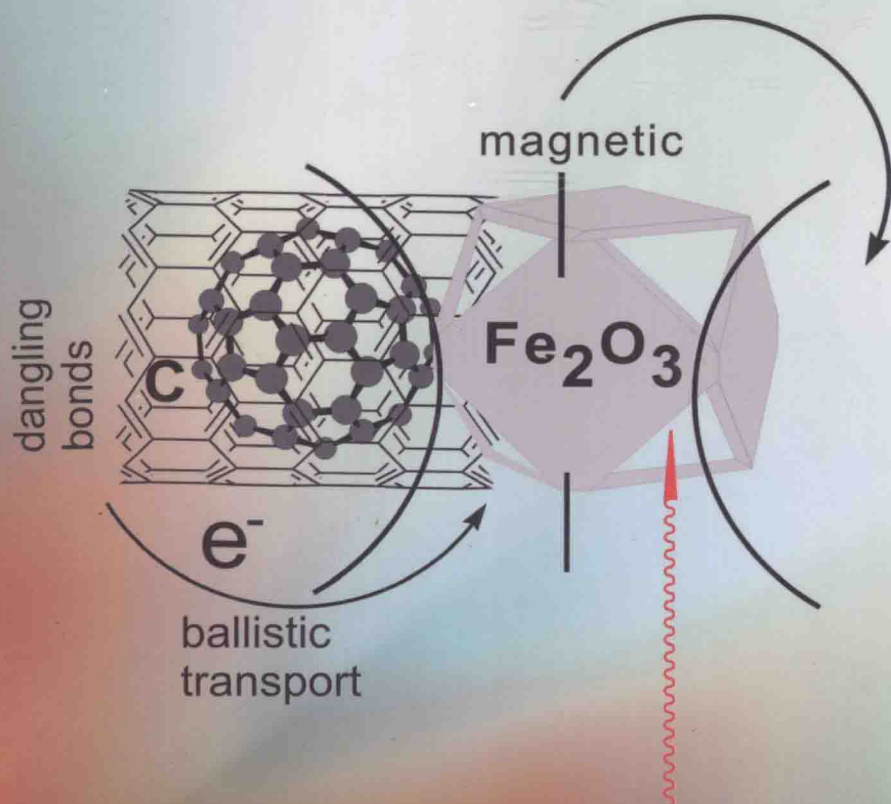


Jurgen Fuhrhop and Tianyu Wang

Metallic and Molecular Interactions in Nanometer Layers, Pores and Particles

New Findings at the Yoctolitre Level



Metallic and Molecular Interactions in Nanometer Layers, Pores and Particles New Findings at the Yoctolitre Level

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Preface

Modern nanochemistry provides the most rewarding and promising opportunity today to re-discover the chemical elements by investigating all their material properties anew under the condition of nanometer confinement. A few chosen examples may help to visualize some of their magic attractions in the 21st century.

Hydrogen and lithium are the lightest reactive elements and serve as electricity sources in fuel cells and laptop batteries. Carbon forms covalent, non-metallic graphite wires, which shows the phenomenon of “ballistic” electron transport without heat. Heavy main group metals like Cs, Bi, Te, and Pb and their combinations with S and Se have a high electric and a low thermal conductivity, a property which leads to a similar cool electric current in thermoelectric nanowires. They are all dream materials for laptop wirings. Crystalline nanolayers of germanium antimony tellurides become amorphous under laser beam pulses within a nanosecond and recrystallize upon electric heating. This behavior became the basis of rewritable laser disks.

The separation of sodium-potassium ions dominates the geological and biological water chemistry. Hydrated sodium ions pile-up in the oceans and in the blood stream, whereas the equally abundant potassium ion is bound to phosphate and silicate nanoparticles of the soil and the protein fibers within muscles and neurons. Main group metal chalcogenides, provide diamagnetic semiconductors which separate electrons and electron holes and luminesce upon charge recombination in nanoparticles. Simple anodic oxidation of metallic aluminum produces regular patterns of nanometer holes coated with alumina and all kinds of brush-like nanowires assemblies may be formed in them and be set free by acid/base treatments.

The most peculiar and important property of transition metals is their variable soft or hard paramagnetism, which is most prominent in thin,

needle-like micro- or nanocrystals. Reversible and long-lived data storage of computers totally rely on optimized magnetic nanodomains.

All of the mentioned material properties strongly depend on confinement and ordering. Crystal surfaces react very differently from bulk crystals, the borderline between fluid layers is a much more favorable environment for nanoparticles than bulk media. Nanoparticles with several organic attachments (dyes, proteins, receptors, DNA *etc*) and asymmetric surface coatings may be constructed and become multifunctional like microorganisms. An organic coating may also stabilize the most fragile nanocrystals like iron metal in air/water environments.

This book provides recent examples for these and many other peculiarities of the artificial nanoworld, which is ordered here by the periodic system of the elements. It helps chemists to think about the development of new material properties, which may improve electronic machines, geological, biological and medical reagents, which may, in the end, be applied worldwide not on the megaton, but on the kilogram scale.

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CHAPTER 1

Atoms, Molecules, Electrons, Light and Heat in Nanometre Confinement

1.1 Introduction

The chemistry within yoctolitre (10^{-24} L) holes or on the surface of particles with a yoctolitre volume is generally called “nanochemistry” because each dimension of these holes and particles measures a nanometre (nm): $1\text{ yL} = 1\text{ nm}^3$. In volumes of up to 1000 yL, *e.g.* $10 \times 10 \times 10\text{ nm}$, all distances between atoms and molecules on the particles or in the holes are within a few nanometres, which allows them to interact with each other and with ions and molecules that approach the surface. Holes left by missing single atoms, molecules or ions in yoctowell walls, and in the centres or surfaces of nanoparticles or nanocrystals, can easily migrate through the whole species.

Yoctolitre dimensions are practical for the estimation of constituent numbers and models based on them: 1 yL can contain ~ 100 metal atoms, 50 molecules of metal oxide (MO), 33 molecules of water or 25 molecules of metal dioxide (MO_2). Nanometre concepts are more appropriate if [111] surfaces have to be compared with [100] surfaces and where vectors, angles, and tenths of an Ångström become important.

The first special property of nanochemistry in or on yoctolitre-sized wells, pores, spheres or crystals depends on the fact that a large percentage of the atoms that form the holes or particles are surface atoms. Quite often the electrons on the hole or nanoparticle surfaces do not bind anything, but represent “dangling bonds” with special activities. The second dominating fact is the relevance of space-dependent physical properties of molecules, which

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play hardly any role in bulk inorganic and organic chemistry. For example, glucose becomes water-insoluble in hydrophobic yoctowells, because the molecules have a hydrophobic edge, which sticks to the wall, and metallic Ag(0) nanocrystals seem to forget about their metallic electron cloud and fluoresce like covalent molecules, for reasons yet unknown.

The translation of stereochemistry into spin interactions of electrons and different kinds of magnetism, the chemical stabilization of electron-hole pairs in order to create luminescence of all colours by the variation of electric potentials, the change in metal crystal lattices on the surface of nanocrystals that renders them catalytically active or fluorescent, and the fixation of water-soluble carbohydrate edge amphiphiles in hydrophobic, water-filled yoctowells are subjects of current research, and chemists interested in the development of new properties should become familiar with them. Research in this field requires access to modern techniques such as rapid crystallization of vapour, laser ablation under water, preparation of atomically smooth surfaces, atomic force microscopy, electron transmission microscopy and electron scanning microscopy, among others.

Subjects covered in this book are, in order of increasing complexity:

- self-cleaning surfaces of nanometre roughness
- quantum dots (QDs), which provide everlasting colours and discrete energy levels instead of bands
- soft and hard magnetic particles for computers and other engineering uses
- minimization of functional AFM tips
- localization of many different single molecules in a very small aqueous space
- decomposition of chlororganic compounds in soils
- coupling of NMR signals with magnetic field steering
- fixation of proteins, DNA and cell surfaces on nanoparticles in water
- routine interconnection of nanoscale elements by nanowiring
- photolysis of water by sunlight
- synthesis of effective catalytic corners with different elements, particularly iron
- assembly of nanoparticles to form efficient thermoelectric elements
- minimization of computer hard disks.

Today's nanochemistry offers a unique chance to have a fresh look at the periodic system of the elements. Carbon chemistry, to name a popular example, is a huge field of classical and modern chemistry, but molecular coatings of nanoparticles that shrink in water on heating, graphite tubes showing ballistic electron transport or the dominance of dangling bonds in nanodiamonds, which makes them extremely reactive, are accessible only through nanochemistry and are of interest in industry and medicine. Magnetic data storage in computer or control devices, the conversion of sunlight into electric currents and of electric currents into light and refrigeration – all these processes depend

on metallic nanoparticles and help to create or replace energy sources. Working with nanocrystals, nanowires and the inner walls of nanometre-wide wells and tubules in university labs will help young scientists to find rewarding problems for work in industry, which has to engineer, optimize, produce, sell and guarantee the nanosized constituents of computers, catalysts, light bulbs, solar converters, *etc.*

Most of the reference citations in this book date from 2005–2009 and are from easily accessible chemical journals. They provide a starting point for learning and research. Each important element of the periodic table has its own section, where relevant general properties are summarized and the element-specific ideas behind recent publications, together with selected results, are discussed. Altogether, the book is as “hands-on” as possible, and we have tried to provide the necessary physical and material chemical background in a descriptive manner. Nanochemists should know whether the products they develop in reaction flasks or on solid surfaces contain magnetic, luminescent or conductive layers, particles or wires.

Our aim is to make readers aware of current developments, while avoiding speculations about economic perspectives. The motivation for “going nano” should always be scientific success, the hope of finding something new and surprising.

1.2 Water, Toluene, Nanoparticles and Nanocrystals

The most useful nanoparticles have diameters between 1 and 10 nm, sometimes up to 20 nm, *i.e.* volumes between one and a few thousands of yoctolitres. The 1 nm species are best for structural and theoretical studies, but 10 nm guarantees relatively high stability and longevity; 5 nm is the standard compromise. Furthermore, all nanosized clusters of atoms or molecules that are of interest fulfil a function. The “functionality” may be as simple as being magnetic, or separation of sodium chloride into Na^+ and Cl^- ions, or as complex as the recognition and removal of two proteins from the bloodstream of a living organism.

We start with water, the lightest natural molecule on Earth with its molecular weight of 18. Its hexameric cluster is the lightest and most dynamic sub-nanoparticle, with a molecular weight of $6 \times 18 = 108$ Da. All molecules that are lighter than water, in particular hydrogen (H_2) and helium (He), eventually disperse into outer space after reaching the atmosphere. Water, however, forms droplets and ice crystallites in the atmosphere which could never escape the gravitational pull of the Earth, even in prebiotic times when the Earth’s surface was volcanic and very hot. Our water molecules originally came here from outer space, but now they never leave the Earth, because they form nanoparticles, micrometre, and millimetre particles at heights of a few hundred metres. Liquid water is the only low-molecular-weight fluid that is stable over a 100 K temperature range. The formation of clusters and droplets has kept water on Earth for more than 4 billion years and allowed for the evolution of life here.

The oxygen atom of water is buried in the centre of a tetrahedron with two electron pairs and two protons at the corners. This polar ordering of the molecular surface dominates the behaviour of fluid and solid water. The oxygen atom holds the protons and electron pairs together, provides weight, and becomes important as molecular triplet oxygen as an end product of the water splitting in photosynthesis. Electrostatic hydrogen bridges between the electron pairs and protons of neighbouring water molecules then form a water pentamer with a molecular weight of 90, which is the unit of larger clusters and finally water droplets (Figure 1.1). But this is not all. In fluid water a sixth water molecule squeezes into the remaining empty space in the fluid pentamer clusters and forms extra hydrogen bridges, which are much less stable than the other four and correspondingly short-lived. It is this sixth molecule that accounts for the low viscosity of water.¹ It moves so quickly from one cluster to another that it keeps them mobile.

The major effect of hydrogen bonding is not viscosity, but high surface tension and boiling point. Bulk water attracts the surface water molecules strongly with one-sided hydrogen bonds, and the air on the upper side cannot compete. We know that 18 cm^3 of water contain 6×10^{23} molecules, so 1 nm^3 or 1 yL of water contains 33 molecules. The hexamer nanoparticle has a volume of

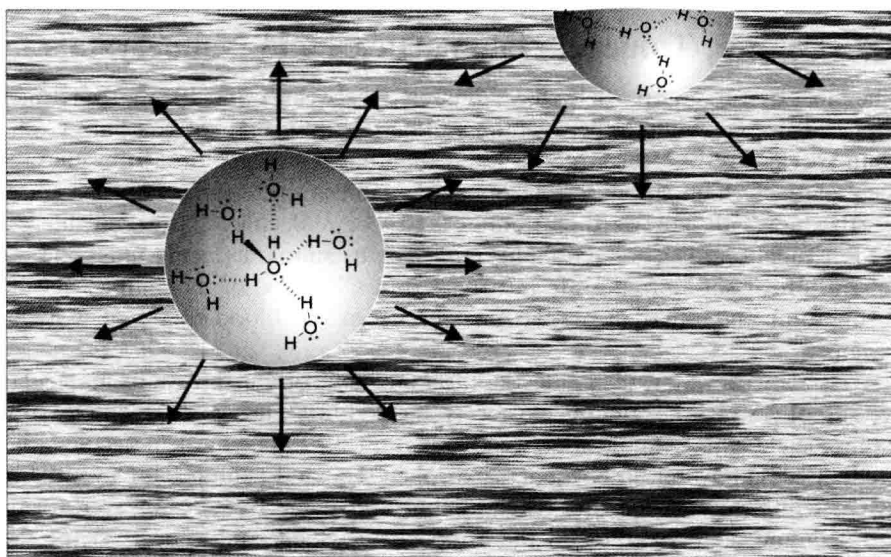


Figure 1.1 In liquid water a pentamer, $(\text{H}_2\text{O})_5$, forms the dynamic building block of large clusters connected by linear hydrogen bonds. $-\text{OH}\cdots\text{O}$. Clustered liquids are usually viscous, *e.g.* glycerol, but water is not. It is fluidized dramatically by a sixth water molecule,^{1a} which enters and leaves the pentamer very fast. Water clusters at the water–air interface are fixated by the internal water, and hardly interact with air. This effect causes surface tension and a high boiling point.^{1b}

only one sixth of a yoctolitre. About 10 molecules of water form the inner hydration sphere of Na^+ and Cl^- ions, and each of the water molecules is part of a cluster. Only one or two NaCl units can thus be dissolved in a 1 yL well, and become centres of fluid water nanoparticles there.

Water is also the basis of life. More than 98% of the molecules of the human body are water, and it participates in each of the molecular actions of proteins, nucleic acids, ATP, *etc.* Its magical role in animal life is the formation of clusters around phosphate, K^+ , Na^+ , and H^+ ions, which permits strong electric potentials in nerves, muscles, brain and stomach.^{1b} The pH of human blood and cellular fluid is always 7.4, which means there is less than 0.01 mg of protons in the whole body with exception of the stomach, with a pH of 0, where there is more than a gram of protons. Enzymes, nerves and muscles for example, would not be active at pH 5.

Soft nanoparticles and nanolayers made of carbon-containing molecules in water, *e.g.* micelles, vesicles and bilayer lipid membranes, are described in Chapter 2. Here we discuss only a few general points about the preparation and properties of metal and metal oxide nanoparticles and nanocrystals.

Toluene (=methylbenzene, $\text{C}_6\text{H}_5\text{CH}_3$) is a water-immiscible solvent. It floats on water, but both water and toluene form 1 nm long fingers, which protrude into each other at the interface for tens of picoseconds (10^{-12} s). Films of Au(0) NPs are formed if a hydrophobic gold(I) compound, namely triphenylphosphine gold chloride, AuPPh_3Cl , is dissolved in the upper toluene phase and a water soluble reductant, formaldehyde, CH_2O , in the form of the polar $\text{P}(\text{CH}_2\text{OH})_4\text{Cl}$ salt, in the water below. Irregular Au_{55} clusters of uniform size (1.2 nm) were then formed at the toluene–water interface and seven such clusters formed a planar heptamer at the interface: one $\text{Au}(0)_{55}$ NP in the centre, six others around it. The lower side of this heptamer became hydrophilic by a water layer, the upper side was hydrophobic with a toluene solvation coat. Now came more gold particles from the water and toluene sides and three of them attach upside to the hydrophobic part, three others downside to the hydrophilic part. They occupied the gaps in the flat Au_{55} heptamer and reverted its polarity. The toluene side now had a hydrophilic surface, the water side a hydrophobic one. The polymeric metal consisted of 13 Au_{55} units. Growth stopped there because the short-lived, 1 nm long toluene fingers in water and water fingers in toluene did not allow for longer reaction times and larger assemblies. Only one NP layer on each side and the solvent caps stabilized the heptamer in the centre. The presence of the clusters and the associated organic layer hindered the progress of the “crystallization” unless the interface was disturbed by surface pressure and/or vibrations (Figure 1.2).²

The primary Au_{55} NPs were also formed in two steps: at first Au_{13} NPs were formed which attached immediately 42 more Au atoms in a second shell. Au_{55} , a “cuboctahedron” with a diameter of 1.2 nm is formed as relatively stable gold core. In the toluene/water case this Au_{55} was surrounded by a non-identified 1.1 nm organic shell, possibly $\text{P}(\text{CH}_2\text{OH})_3$ /toluene, and the coated Au_{55} NPs again clustered to form the described cluster of 13 Au NPs of 2.3 nm diameter

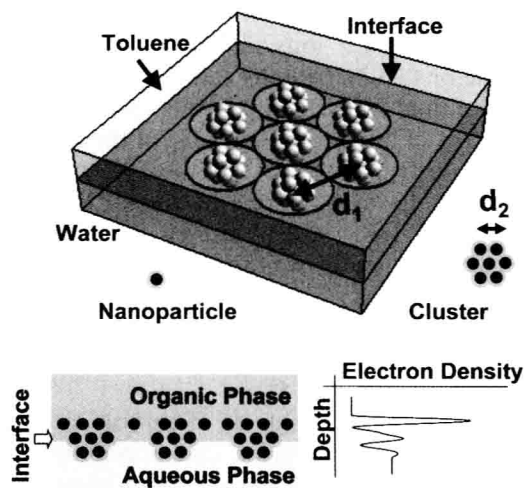


Figure 1.2 3D schematic of a 13-membered capped gold nanoparticle cluster and 2D model of three such clusters in water and toluene fingers.²

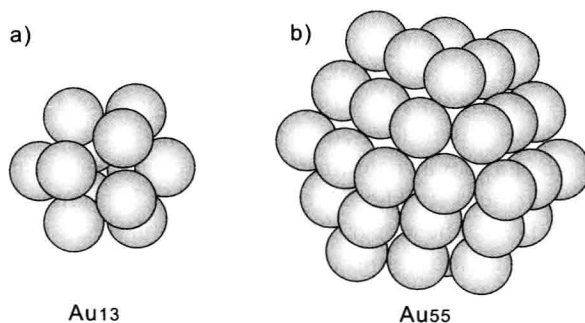


Figure 1.3 The primary nanocrystals of Au(0), namely Au₁₃, Au₅₅ and (Au₅₅)₁₃.² Attempts to purify and isolate Au₅₅ failed.

each, one in the centre and 12 on the surface (Figure 1.3). Such interfacial assemblies are presumably standard intermediates in the formation of very small spherical NPs. Solidification of vapours on cold surfaces, laser ablation under water or rapid precipitation in acid/base reactions in uniform solvents probably produce the same intermediates but limitation of growth is caused there by short crystallization times, rather than by “fingers” between two phases.

The major crystal lattices of metals are summarized in a general structure proposed by Hume and Rothery (Figure 1.4). The possible positions of the atoms are identified by the letters *a*, *b*, *c* and *d*. If all positions are occupied by the same kind of atoms, e.g. Fe(0), the structure is cubic close packed (ccp). The Hume–Rothery figure contains eight of these ccp units and occurs in nature in