GLIMPSES OF NANOTECHNOLOGY

PART-I

“Nanomaterials: Synthesis and Current Researches”

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I. INTRODUCTION

What are Nanoscience and Nanotechnologies?

Nanotechnology is engineering at the atomic or molecular (group of atoms) level. It is a group of enabling technologies that involve the manipulation of matter at the nanoscale (generally accepted as 100 nanometres or less) to create new materials, structures and devices. At this very small scale, the chemical and physical properties of materials can change, such as colour, magnetism and the ability to conduct electricity. Nanotechnology research and its applications have been growing rapidly worldwide for the past decade, with an increasing number of nanotechnology products becoming commercially available. These include nanoscale materials, powders, solutions and suspensions of nanoscale materials as well as composite materials and devices having a nanostructure. Nanotechnology, its products and applications have the potential to offer significant social and environmental benefits. For example, it is anticipated that nanotechnology will lead to new medical treatments and tools, more efficient energy production, more effective pollution reduction, and stronger, lighter materials. The potential benefits of nanotechnology to industry and the community in general have been highlighted in several reports. However, there are concerns that some applications and products of nanotechnology may present health, safety and environmental hazards and risks. Nanotechnology can be either a ‘top-down’ technique, such as etching and milling of larger material, or a ‘bottom-up’ technique that involves assembling smaller subunits to produce the nanoscale product.

The first term of reference of this study was to define what is meant by nanoscience and nanotechnology. However, as the term ‘nanotechnology’ encompasses such a wide range of tools, techniques and potential applications, we have found it more appropriate to refer to ‘nanotechnologies’. Our definitions were developed through comments received from the scientists and engineers and through the study of websites. Although there is no sharp distinction between them, in this report we differentiate between nanoscience and nanotechnologies as follows.

The prefix ‘nano’ is derived from the Greek word for dwarf. One nanometre (nm) is equal to one-billionth of a metre, 10–9m. A human hair is approximately 80,000nm wide, and a red blood cell approximately 7000nm wide. Figure 2.1 shows the nanometre in context. Atoms are below a nanometre in size, whereas many molecules, including some proteins, range from a nanometre upwards. The conceptual underpinnings of nanotechnologies were first laid out in 1959 by the physicist Richard Feynman, in his lecture ‘There’s plenty of room at the bottom’ (Feynman 1959). Feynman explored the possibility of manipulating material at the scale of individual atoms and molecules, imagining the whole of the Encyclopaedia Britannica written on the head of a pin and foreseeing the increasing ability to examine and control matter at the nanoscale.

The term ‘nanotechnology’ was not used until 1974, when Norio Taniguchi, a researcher at the University of Tokyo, Japan used it to refer to the ability to engineer materials precisely at the nanometre level (Taniguchi 1974). The primary driving force for miniaturisation at that time came from the electronics industry, which aimed to develop tools to create smaller (and therefore faster and more complex) electronic devices on silicon chips. Indeed, at IBM in the USA a technique called electron beam lithography was used to create nanostructures and devices as small as 40–70nm in the early 1970s.

The size range that holds so much interest is typically from 100nm down to the atomic level (approximately 0.2 nm), because it is in this range (particularly at the lower end) that materials can have different or enhanced properties compared with the same materials at a larger size. The two main reasons for this change in behaviour are ***an increased relative surface area, and the dominance of quantum effects***. An increase in surface area (per unit mass) will result in a corresponding increase in chemical reactivity, making some nanomaterials useful as catalysts to improve the efficiency of fuel cells and batteries. ***As the size of matter is reduced to tens of nanometres or less, quantum effects can begin to play a role, and these cansignificantly change a material's optical, magnetic or electrical properties.*** In some cases, size-dependent properties have been exploited for centuries. For example, gold and silver nanoparticles (particles of diameter less than 100 nm; see section 3.2) have been used as coloured pigments in stained glass and ceramics since the 10th century AD (Erhardt 2003). Depending on their size, gold particles can appear red, blue or gold in colour. The challenge for the ancient (al)chemists was to make all nanoparticles the same size (and hence the same colour), and the production of single-size nanoparticles is still a challenge today.

At the larger end of our size range, other effects such as surface tension or 'stickiness' are important, which also affect physical and chemical properties. For liquid or gaseous environments Brownian motion, which describes the random movement of larger particles or molecules owing to their bombardment by smaller molecules and atoms, is also important. This effect makes control of individual atoms or molecules in these environments extremely difficult. Nanoscience is concerned with understanding these effects and their influence on the properties of material. Nanotechnologies aim to exploit these effects to create structures, devices and systems with novel properties and functions due to their size.

In some senses, nanoscience and nanotechnologies are not new. Many chemicals and chemical processes have nanoscale features – for example, chemists have been making polymers, large molecules made up of tiny nanoscalar subunits, for many decades. Nanotechnologies have been used to create the tiny features on computer chips for the past 20 years. The natural world also contains many examples of nanoscale structures, from milk (a nanoscale colloid) to sophisticated nanosized and nanostructured proteins**.**

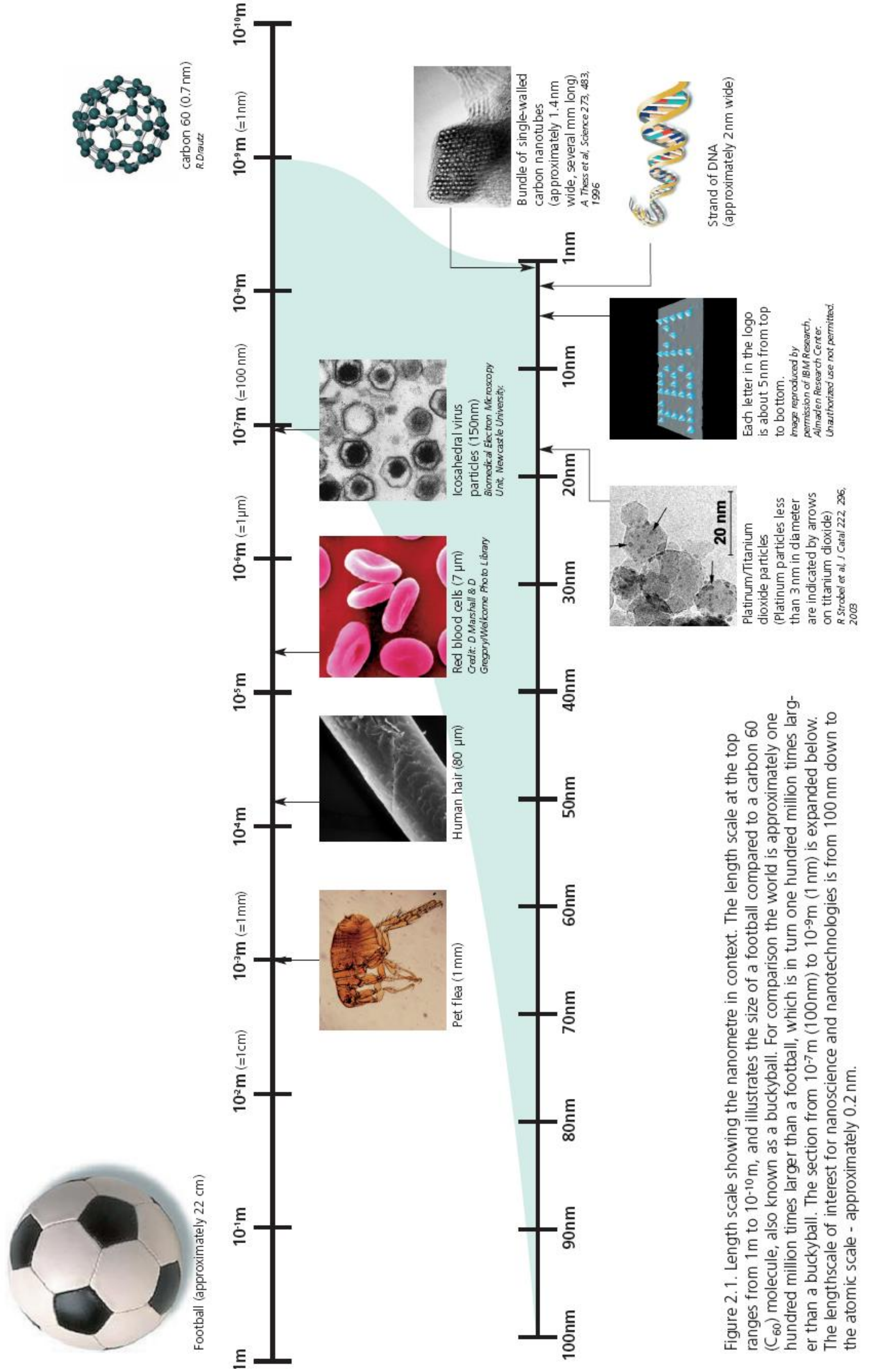

Figure 2.1. Length scale showing the nanometre in context. The length scale at the top ranges from 1m to 10^{-10}m, and illustrates the size of a football compared to a carbon 60 (C_{60}) molecule, also known as a buckyball. For comparison the world is approximately one hundred million times larger than a football, which is in turn one hundred million times larger than a buckyball. The section from 10^{-7}m (100nm) to 10^{-9}m (1 nm) is expanded below. The lengthscale of interest for nanoscience and nanotechnologies is from 100 nm down to the atomic scale - approximately 0.2 nm.

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Definitions of nanoscience and nanotechnologies

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.

Nanotechnologies are the design, characterisation, production and application of structures, devices and systems by controlling shape and size at nanometre scale, biological activities, such as flexing muscles, releasing energy and repairing cells. Nanoparticles occur naturally, and have been created for thousands of years as the products of combustion and food cooking. However, it is only in recent years that sophisticated tools have been developed to investigate and manipulate matter at the nanoscale, which have greatly affected our understanding of the nanoscale world.

A major step in this direction was the invention of the scanning tunnelling microscope (STM) in 1982, and the atomic force microscope (AFM) in 1986. These tools use nanoscale probes to image a surface with atomic resolution, and are also capable of picking up, sliding or dragging atoms or molecules around on surfaces to build rudimentary nanostructures. These tools are further described in Box 3.1. In a now famous experiment in 1990, Don Eigler and Erhard Schweizer at IBM moved xenon atoms around on a nickel surface to write the company logo (Eigler and Schweizer 1990) (see Figure 2.1), a laborious process which took a whole day under well-controlled conditions. The use of these tools is not restricted to engineering, but has been adopted across a range of disciplines. AFM, for example, is routinely used to study biological molecules such as proteins.

The technique used by Eigler and Schweizer is only one in the range of ways used to manipulate and produce nanomaterials, commonly categorised as either ‘top-down’ or ‘bottom-up’. ‘Top-down’ techniques involve starting with a block of material, and etching or milling it down to the desired shape, whereas ‘bottomup’ involves the assembly of smaller sub-units (atoms or molecules) to make a larger structure.

Nanotechnologies can be regarded as genuinely interdisciplinary, and have prompted the collaboration between researchers in previously disparate areas to share knowledge, tools and techniques. An understanding of the physics and chemistry of matter and processes at the nanoscale is relevant to all scientific disciplines, from chemistry and physics to biology, engineering and medicine. Indeed, it could be argued that evolutionary developments in each of these fields towards investigating matter at increasingly small size scales has now come to be known as ‘nanotechnology’.

Nanoscience and nanotechnologies encompass a broad and varied range of materials, tools and approaches. Apart from a characteristic size scale, it is difficult to find commonalities between them. We should not therefore expect them to have the same the same health, environmental, safety, social or ethical implications or require the same approach to regulation.

What are Nanomaterials?

Engineered nanomaterials are materials designed at the molecular (nanometre) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts.

The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviours. Nanomaterials have extremely small size as their defining characteristic, although there is as yet no agreed national or international definition for nanomaterials. The current working definition of nanomaterials is a material having at least one dimension 100 nanometres or less. To put nanomaterials into perspective, up to 10,000 could fit across a human hair. Nanomaterials can be nanoscale in one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Products containing engineered nanomaterials are already in commercial use, with some having been available for several years or decades.

Our Hopes for Nanotech: Environmental Benefits

Fig. 2a. Nanomaterials commercial use.

The range of commercial products available today is very broad, including stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints and varnishes. Nanocoatings and nanocomposites are finding uses in diverse consumer products, such as windows, sports equipment, bicycles and automobiles. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls using butyl rubber/nano-clay composites. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and selfcleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings.

Marketplace Presence
Creates Urgency

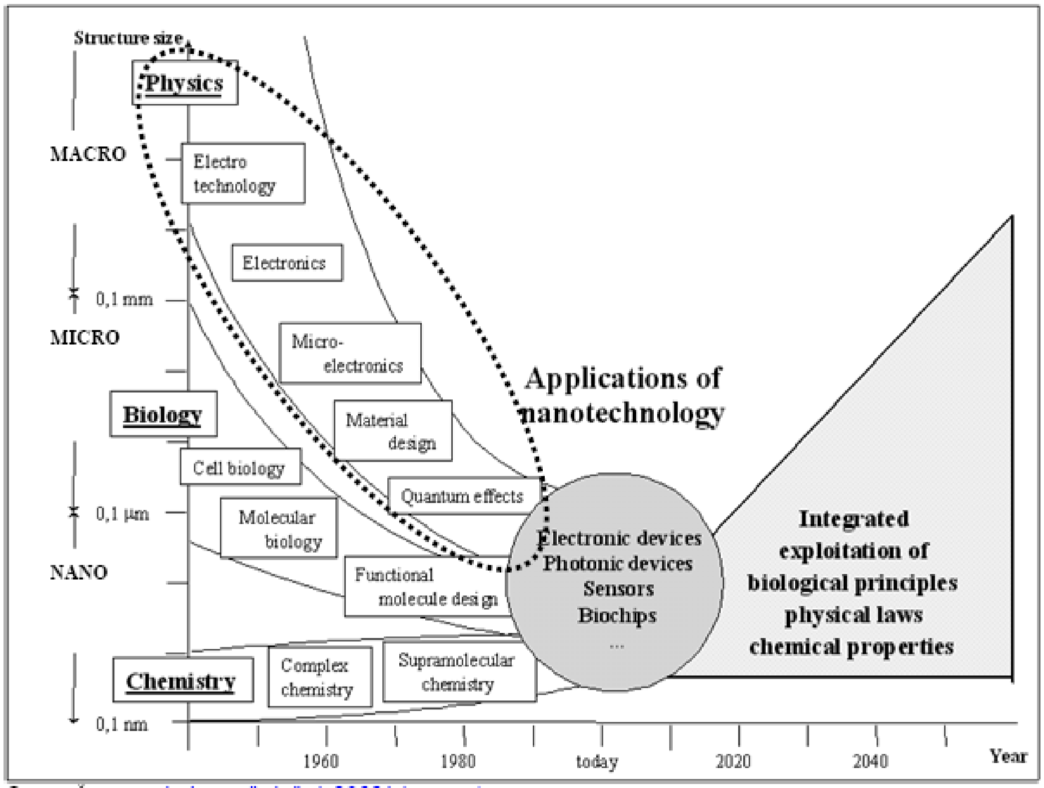
Fig. 2b. Nanomaterials commercial use.

The main challenge for top-down manufacture is the creation of increasingly small structures with sufficient accuracy, whereas for bottom-up manufacture, it is to make structures large enough, and of sufficient quality, to be of use as materials. These two methods have evolved separately and have now reached the point where the best achievable feature size for each technique is approximately the same, leading to novel hybrid ways of manufacture.

Definitions, nomenclature and characterisation:

For toxicity testing and exposure measurement of nanomaterials, it is important to adequately characterise the materials. Chemical and physical properties that may be important for characterising nanomaterials include size, size distribution, surface area, shape, chemical composition and agglomeration state, though their importance will vary for different types of nanomaterials.

It is probable that new methods will be required to characterise these properties. There is also an overarching need for internationally agreed nomenclature for nanomaterials and nanoparticles, to facilitate harmonised descriptions of the materials and to eliminate ambiguities.



Source[3]: www.sigda.org/iwls/iwls2002/elena.ppt

Fig. 3. Applications of Nanotechnology

Priority needs for Nanomaterials

There is insufficient knowledge concerning the characterisation, use and exposure, fate and persistence, toxicology and ecotoxicology of nanomaterials, to allow for adequate assessment of the risks of nanomaterials. The difficulty in collecting this information is compounded by the current lack of uniform internationally accepted nomenclature for nanomaterials, and the absence of standard methods for their characterisation and measurement. Several reviews have identified the following key areas that require further research to enable adequate risk assessment and regulation of nanomaterials.

Markets

With an annual growth rate of some 15% over the past three decades, the global microelectronics industry has become a central strategic enabler for the entire global economy, surrounding us in our daily lives as an essential constituent of a huge range of products and services: cars, phones, medical systems, multimedia applications, to name but a few since computing power is embedded in most products today. **Current investment** in electronics accounts for some 30% of overall industrial investment in the developed world. The microelectronics value chain – from the semiconductor chip manufacturers together with their equipment and materials suppliers to the large set of related industries, such as design houses, systems builders and integrators – represent nearly 1% of global gross domestic product (GDP). In Europe alone, some 40% of the **annual sales** of the semiconductor manufacturers are reinvested in R&D and improved production processes. As a direct result, the worldwide annual market for electronics at just under €800 billion is now bigger even than the global automotive market.

When the many other industries that depend on electronics – telecommunications, Internet services and consumer products to the defence and aerospace industries – are included, the **global value** leverages some €5,000 billion Worldwide production of transistors reached $1x10^{18}$ or a million, million, million ‘gates’ in 2003. By 2015, it is forecast that industry will need capabilities to manufacture the equivalent of 10 million silicon transistors per human being per day in the developed world. For example, estimates for 2007 already indicate an increase over 2003 in demand for DVDs by 50 to 55%, digital televisions by 30 to 40%, mobile phones by 45 to 50% and personal computers by 35 to 40%. This in itself will lead to a much greater need for nanoelectronics design and manufacturing capabilities, and increased opportunities.

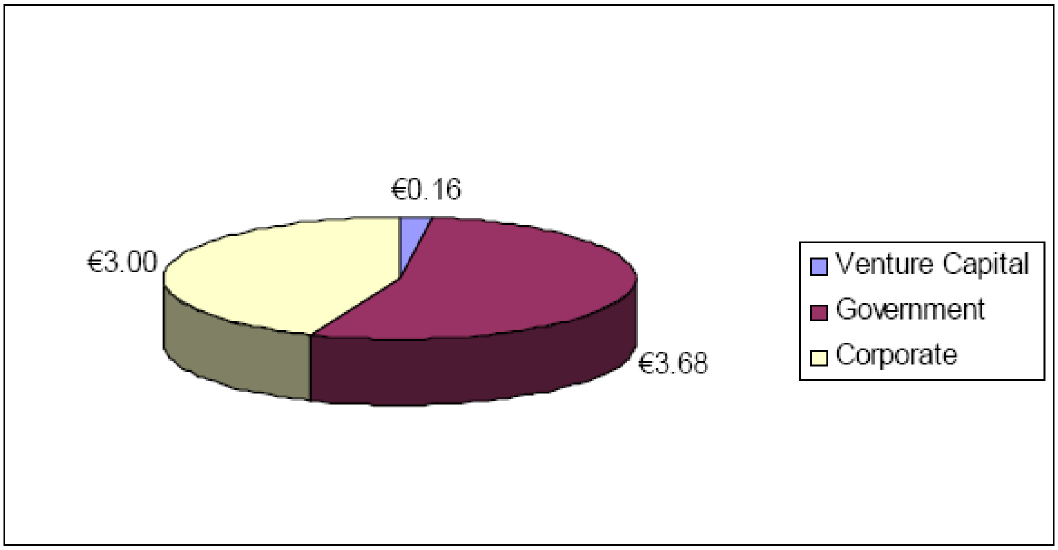
The market analyst firm NanoMarkets, forecasts that the worldwide plastic electronics market will grow to US$5.8 billion (€ 4.6 billion) in 2009, and reach US$23.5 billion (€18.8 billion) by 2012. In 2009, Nano Markets expects that:

- displays will account for 46 percent of the plastic electronics market
- memory will account for 38 percent and
- 37 percent of plastic electronics products will come from the mobile phone sector.

Options and Opportunities

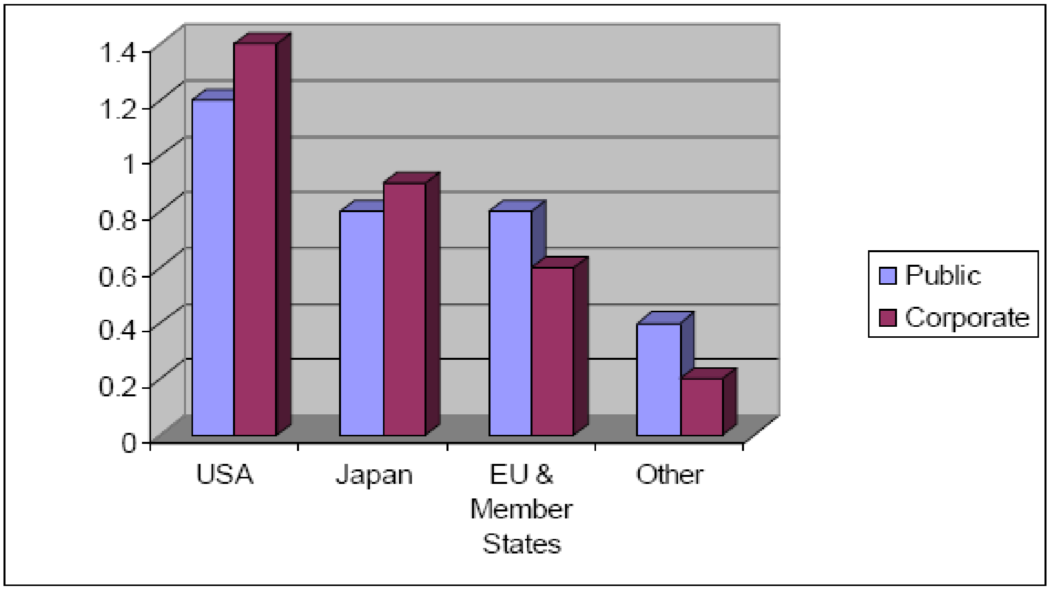
The global investment in nanotechnology and nanoelectronics is increasing annually. The National Science Foundation has brought forward their forecast from 2015 to 2010, valuing the nanotechnology industry to be worth US$ 1 trillion.

Investment and values in nanoelectronics need to be placed in context of overall investments and values of the field of nanotechnology as a whole. During 2004 the global funding of nanotech was €6.48 billion. The levels of investments by various public and private finance sources are indicated in figures 4 and 5. l €0.16 €3.68 €3.00 Venture Capita Government Corporate **Current investment in electronics accounts for** some 30% of overall industrial investment in the developed world. The **market size** of the nanoelectronics business chain (manufacturers, related industries such as the equipment and material suppliers, the



Source: Nordan, MM et al.. 2005. Nanotechnology: Where does the U.S. stand? Luxresearch. June 29, 2005. NPS-01-001.

Figure 4 - Global funding of nanotechnology R&D - 2004 (x€billion)



Source: Nordan, MM et al.. 2005. Nanotechnology: Where does the U.S. stand? Luxresearch. June 29, 2005. NPS-01-001.

Figure 5 - Corporate and public funding of nanotechnology R&D - 2004 (x€billion).

designers, system builders and integrators, etc.) represents currently nearly 1% of the world wide GDP with a strong annual average growth rate of approximately 15%. When considering the leverage effect of this enabling technology (telecom operators, consumer products, internet services, automotive, defence, space, etc.), its **global value** can be increased to an estimated €5,000 billion. Furthermore, the nanoelectronics sector is also a significant generator of highly qualified jobs, given its manufacturing dimension.

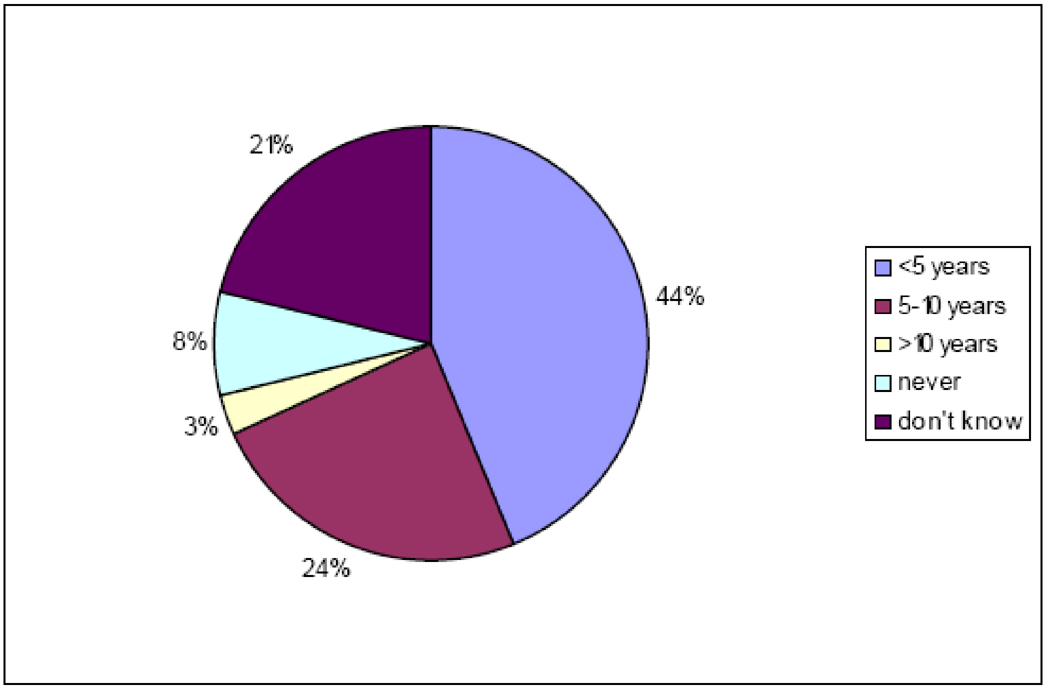
In Europe some 40% of the **annual sales** of the semiconductor manufacturers are reinvested in R&D and improved production processes. The worldwide annual market for electronics at just under €800 billion is now bigger even than the global automotive market. European Nanoelectronics Initiative Advisory Council (ENIAC) has stated that for Europe to become the world's most competitive powerhouse, Europe must lead the transition of the micro-electronics sector to the next generation of nano-electronics, with co-ordinated public and private investments of at least €6 billion per year. This is the message from CEOs of leading companies and research organisations also emphasised that smarter and smaller electronics at the nanometer scale, managing vast amounts of data, are becoming key components for many applications, from household appliances and consumer goods to automotive transport, health care and security, and ultimately ambient intelligence.

Each **new technological generation** requires a steep increase in the level of investment needed to conduct research and build production plants – the European electronics industry currently spends 20% of turnover on research and a typical fabrication facility today costs around €2.5 billion. Nano Markets, a leading advanced technology analyst firm based in the US, forecasts that the market for nano-enabled electronics will reach US$10.8 billion (€8.6 billion) in 2007 and grow to US$82.5 billion (€66 billion) in 2011.

Education and Skills

The electronics industry generates the type of highly skilled employment that is essential for the future social and economic well-being in individual EU Member States and Europe as a whole. Nanoelectronics offers the national and European electronics sector the opportunity of becoming an even more significant generator of jobs for highly qualified personnel. The increasing complexity of the technology requires significant **multidisciplinary education and training** programmes. Demand is already outstripping the supply of skills. The way to educate and retain future technology leaders is to ensure that state-of-the-art education and research infrastructures are available and that most of the high-value-creating industrial activities of the total value chain are located within Europe.

In a recent study on the future availability of trained staff in nanotechnology, 44% of participants predicted a **shortage in nanopersonnel** within 5 years, while a further 24% expected a shortage within 10 years. It will be reasonable to assume a similar pattern to occur in the nanoelectronics personnel availability (Figure 6).



Source: NanoForum, 2004.

Figure 6 - Expected shortage of trained staff in nanotechnology.

The technology research programmes also require educated multidisciplinary staff as well as system architects, giving rise to a need for curricula delivering new profiles of expertise to avoid bottlenecks in development. These should be introduced into undergraduate and graduate courses so that qualified people are available to undertake research and development enabling new products and applications to be designed and manufactured.

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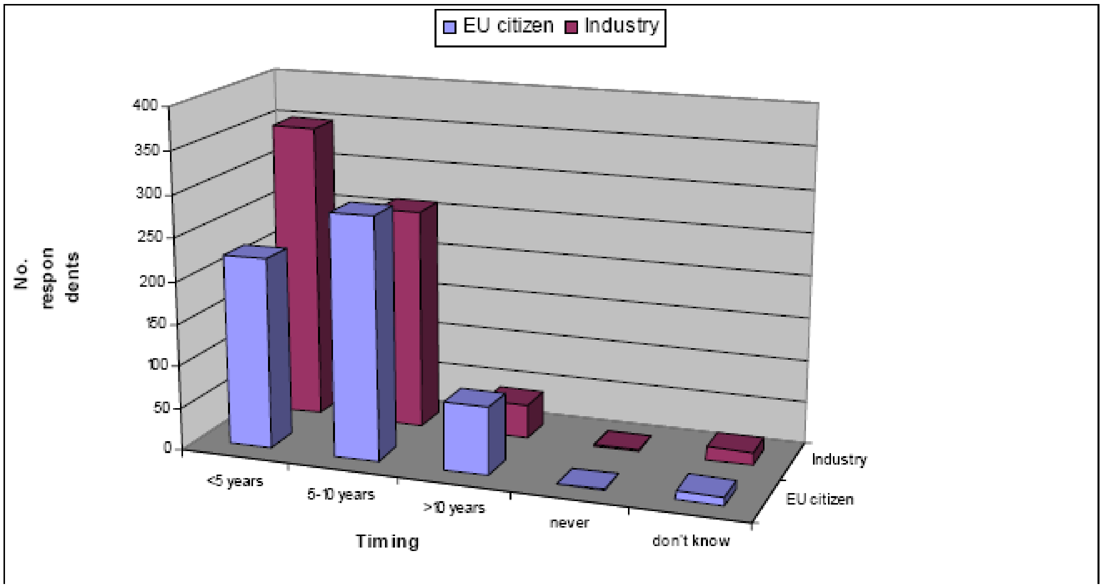
II. Social and Economic Issues Related to Nanotechnologies

II. SOCIAL AND ECONOMIC ISSUES RELATED TO NANOTECHNOLOGIES

Notable recent success stories – mobile telephones, digital media, computing and networking (especially the Internet), safer and more efficient vehicles with less-polluting engines, and medical systems – illustrate the crucial **innovative role** that microelectronics has played. The move from micro- to nanoelectronics can only increase this key position. Microelectronics has become a foremost driver of **social and economic progress** worldwide. With an average annual growth of 15% a year for the past three decades, its industry has made massive investments, creating thousands of jobs. This trend expected to continue.

The electronics industry is continuing to develop. The quantity of products is increasing, consumption patterns are changing and both environmental science and technology are continuing to evolve. The **regulatory framework** therefore needs to be adapted continuously in close consultation with industry, society and policy-makers. Europe is leading the way with legislation already in place to address and appropriately manage environmental risks arising from production, use and disposal of electronic products – from the collection and recycling of electrical and electronic waste to the development of lead-free solders.

The impact of nanoelectronics on **personal security and privacy** will also have to be taken into account. New technology will offer low-cost and user-friendly embedded security but this will pose privacy questions as nanotechnologies allow tagging, tracing and data collection on a large scale. This demands research on new technical, regulatory and ethical solutions.



Source: NanoForum 2004.

Figure 7 - Expected time span in which nanotechnology will affect society and industry.

A key aspect of collaborative research programmes in this field must be to raise **public awareness** of nanoelectronics industries and products among politicians and the public at large. A recent survey on the impact of nanotechnology indicated that the majority of respondents expect that nanotechnology will affect industry within the next five years and society within the next ten years (Figure 7). In general, the awareness is growing internationally, among policy-makers, scientists and industry representatives alike that more and better knowledge on future impacts of NT and considerable research efforts in this field are needed. Several studies have indicated that **public awareness of nanotechnology** in general and of its implications is basically nonexistent at the moment. If fears and resentments towards NT arise in society, these can induce negative effects such as drawbacks in nanotechnology research and commercialisation. Even within **science and industry** the awareness and understanding of the impacts of NT research and development is quite limited among researchers and engineers. Yet, only a fairly small community mainly consisting of social scientists deals with the assessment and evaluation of NT research, development and application.

Do Nanomaterials pose health and/or environmental risks?

Concerns have been raised about potential health and environmental ipacts of nanomaterials. This is principally because of their small size and novel properties and because research in experimental animals and in vitro systems on some nanomaterials has indicated potential environmental and health effects. Almost all concerns have related to free, rather than fixed nanomaterials. There has been little research into the potential hazards (health, safety and environmental effects) of these materials, their exposure, fate or persistence or the risks to people or the environment exposed to them. Due to this lack of information, there are many uncertainties as to whether nanomaterials pose or are likely to pose health and environmental risks. However, the body of data is increasing, as more organisations research the health and environmental aspects of nanomaterials. For example, there is a great deal of ongoing research into nanoscale metal oxides, carbon nanotubes, fullerenes and quantum dots.

Hazards

The same properties that nanomaterials are designed to exhibit are also properties that may cause nanomaterials to present human health and environmental hazards. For example, with decreasing particle size, the surface area to mass ratio becomes greater.

What We Want to Avoid:
The “Wow- to-Yuck” Trajectory

Technology	Promise	Problem
Asbestos	Insulator, fire retardant	Lung disease; carcinogen
DDT	Mosquito and malaria control	Persistent, bioaccumulative, toxic;
Leaded gas	Engine improvements	Persistent, bioaccumulative, toxic; Carcinogen; developmental toxin
PCBs	Insulator, fire retardant	Persistent, bioaccumulative, toxic; Probable human carcinogen; Multiple other probable toxic effects
CFCs	Refrigerant, aerosol	Ozone depletion
GMOs	Improved crop yields	Public backlash; inadequate controls

Can we get it right the first time with nanotech?

Fig.8. Problems related to Nanomaterials

This means that there are potentially more atoms on the surface area to react with the environment and other substances. High reactivity is a desired property for many intended applications of nanomaterials, such as catalysts, however, this increased reactivity can lead to greater toxicity for cells and living organisms. The physicochemical properties of nanomaterials are determined by the chemical composition, surface structure (including surface coatings), small size and associated increase in surface to volume ratio, solubility, shape and aggregation. The influences of physicochemical properties on the toxicological and eco-toxicological profile of nanomaterials are not yet fully understood. Changes in physicochemical properties can also increase the potential for some nanomaterials to exhibit fire and/or explosion hazards or catalytic activity.

Limited data from preliminary studies in experimental animals have shown that some nanomaterials can accumulate in the lungs and translocate to the blood, cross the blood-brain barrier, and produce inflammatory responses and are capable of direct interaction with DNA in vitro. Parallels have also been drawn with the incidentally produced nanoparticles (such as ultrafine particles in diesel exhaust and other combustion products) and their associated adverse health effects. To date, there have been no confirmed reports of adverse effects to humans or the environment as a result of exposure to engineered nanomaterials.

In summary, little is known about the toxicology of nanomaterials, though early indications are that some nanoscale materials have greater reactivity than their bulk counterparts. Based on the limited data that are available, there are concerns that the adverse effects of nanomaterials cannot be reliably predicted or derived from the known toxicity of the bulk material.

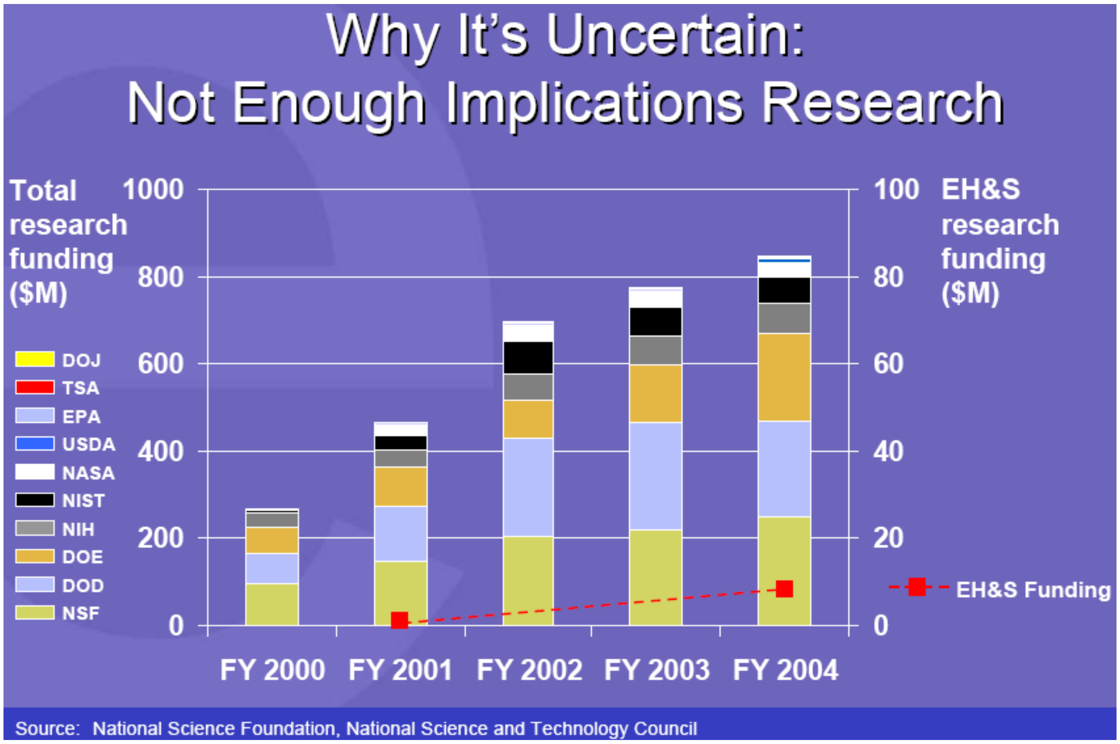
Hazards to human health and the environment:

There is a clear need for more data to understand the hazards that nanomaterials may present to human health and the environment. The existing standard test methods may not be adequate to identify some of the hazards of nanomaterials. Methodologies for assessing toxicological endpoints may need to be developed or existing toxicity tests adapted. There is also a need to review testing strategies and base datasets for human and environmental hazards and evaluate their adequacy to identify the potential hazards of different types of nanomaterials.

Exposure

There is a need for data on use and potential sources of exposure to nanomaterials, their fate and behaviour. Methodologies to measure human and environmental exposure may need to be adapted or new ones developed to account for the different characteristics considered to be important for nanomaterials.

Factors determining human and environmental exposure include the extent and pattern of use, the exposure pathway and fate and behaviour of the nanomaterial. While reported applications of nanomaterials are diverse, there are very little data on actual uses and applications, thus increasing the difficulty of determining exposure in Australia. Some nanomaterials are designed for use in solution or suspension, others are immobilised in (or on the surface of) other materials, while some applications may require the nanomaterial to be used in an unconstrained form.



Source: National Science Foundation, National Science and Technology Council

Fig.9.Uncertain Implications.

There is potential for exposure to humans (workers and the public) and the environment during manufacture, use and disposal of nanomaterials, but it is difficult to identify and quantify at present.

Nanomaterials are orders of magnitude smaller than conventional bulk materials, and therefore may result in an increased dose, due to a greater capacity for absorption, and potential for translocation within the body and/or access to cells. Information on routes of exposure, movement or translocation of materials once they enter the body and interaction of materials with the body's biological systems are largely unknown. Due to differences in physical and chemical properties, the fate, persistence and behaviour (such as agglomeration) of nanomaterials may differ from the bulk material and lead to a greater potential for increased exposure and dose.

What is being done internationally?

International activities:

Risk assessment of nanomaterials has become the focus of increased international attention. International agencies and individual governments, research teams and industry are actively working to produce, gather and share information to assist in formulating appropriate approaches to the regulatory challenges posed by nanotechnology and nanomaterials. For example, the OECD Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology has started work in the area of risk assessment of nanomaterials. The OECD recognises that there should be a coordinated approach towards ensuring the safety of nanomaterials in order to help realise the benefits of nanotechnology. The OECD Chemicals Joint Meeting is considering establishing a Working Group to address issues such as international co-ordination in regulatory approaches; development of assessment methodologies and testing schemes; and information sharing and exchange in risk assessment and management. There is also increasing activity within the international standards community to address standardisation and nomenclature issues arising from the development of nanotechnology. The International Standards Organisation ISO/TC 229, Nanotechnologies, held its inaugural meeting in November 2005. A number of institutions have published reports discussing the potential environmental, safety and health risks associated with the manufacture, use and distribution of nanomaterials, including the UK Royal

Society with the Royal Academy of Engineering, the UK Department for Environment Food and Rural Affairs, the US Environmental Protection Agency, the US National Institute for Occupational Safety and Health, the Woodrow Wilson International Center for Scholars. These reports are varied in approach and scope and are useful sources of information (see attached list).

NICNAS activities

While nanomaterials have the potential to provide significant benefits to society, it is important to ensure they are introduced safely. It is timely that NICNAS considers nanomaterials and their potential health and environmental impacts.

The challenge for NICNAS is to ensure the regulatory framework can adequately identify and assess any risks of nanomaterials, and that there are appropriate mechanisms for the management of the risks. The current needs of regulators, in order to encourage the safe development of nanotechnology while ensuring the health and safety of the community at work, in the marketplace and in the environment, are many. Therefore, national and international collaboration is important to address issues of mutual benefit, such as nomenclature, measurement, standardisation, and common approaches to risk assessment.

Activities NICNAS is currently undertaking include:

- Issuing of a voluntary call for information for nanomaterials, seeking information on uses and quantities of nanomaterials imported or manufactured for industrial uses, including use in cosmetics and personal care products.
- This information will assist in understanding which nanomaterials are available on the market or close to commercialisation, and in focussing our efforts to ensure the adequacy of the regulatory scheme. NICNAS will analyse the information and prepare a report on the extent and scope of the use of nanomaterials in industrial, cosmetic and personal care products in Australia. This information will in turn assist in prioritising regulatory considerations to ensure these nanomaterials can be introduced safely.
- Monitoring relevant new chemical notifications will help NICNAS to identify research areas and to focus on ensuring it can adequately address safety issues for nanomaterials.

- Working with the Department of Health and Ageing and other government agencies and departments to ensure a nationally consistent approach to regulation of nanomaterials in keeping with COAG principles of good regulation. NICNAS is a member of interdepartmental committees providing advice to the National Nanotechnology Taskforce.
- Engaging the chemical industry and the community through the active participation in discussions on nanomaterials, such as with

NICNAS's Industry Government Consultative Committee, and Community Engagement Forum.

- Participating in relevant national efforts, including the Standards Australia Nanotechnologies Committee (NT-001), to ensure a consistent approach in standards setting and to promote sharing of information.
- Taking an active role in international activities, such as the OECD Steering Committee on Safety of Manufactured Nanomaterials, to develop appropriate regulatory standards for nanomaterials and developing best practice testing protocols and risk assessment methodologies.
- Maintaining a watching brief on outcomes of research being undertaken on the health, safety and environmental aspects of nanomaterials.

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III. Methods for the Synthesis Of Nanoparticles and Nanomaterials

III. METHODS FOR THE SYNTHESIS

OF NANOPARTICLES AND NANOMATERIALS

Synthesis and assembly strategies of nanoparticles and nanomaterials accommodate precursors from liquid, solid, or gas phase. They employ both chemical and physical deposition approaches; and similarly rely on either chemical reactivity or physical compaction to integrate nanostructure building blocks within the final material structure. The variety of techniques is shown schematically in Figure 1. The "bottom-up" approach of nanomaterials synthesis first forms the nanostructured building blocks (nanoparticles) and then assembles them into the final material. An "ample of this approach is the formation of powder components through aerosol techniques and then the compaction of the components into the final material..

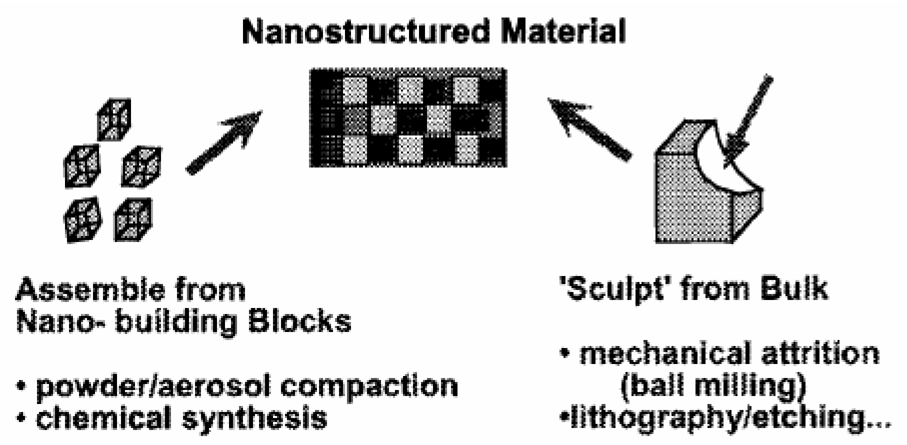


Figure l0. Schematic of variety of nanostructure synthesis and assembly approaches. pattern transfer processes (such as reactive ion etching) that have the requisite spatial resolution to achieve creation of structures at the nanoscale.

These techniques have been used extensively in the formation of structural composite nanomaterials. One "top-down" approach begins with a suitable starting material and then "sculpts" the functionality from the material This technique is similar to the approach used by the semiconductor industry in forming devices out of an electronic substrate (silicon), utilizing pattern formation (such as electron beam lithography) and This particular area of nanostructure formation has tremendous scope and is a driving issue for the electronics industry. Another top-down approach is "ball-milling," the formation of nanostructure building blocks through controlled, mechanical attrition of the bulk starting material. Those nano building blocks are then subsequently assembled into a new bulk material. In fact, many current strategies for material synthesis integrate both synthesis and assembly into a single process, such as characterizes chemical synthesis of nanostructured materials. The degree of control required over the sizes of the nanostructure components, and the nature of their distribution and bonding within the fully formed material varies greatly, depending on the ultimate materials application. Achieving selective optical absorption in a material may allow a wide range of sizes of the component nanostructure building blocks, while quantum dot lasers or single electron transistors require a far tighter distribution of size of the nanostructure components. Compaction methods may provide excellent adhesion for nanocomposite materials of improved structural performance (e.g., ductility), but such interfaces may not be satisfactory for electronic materials.

The intention of this chapter is not to recapitulate in detail the various synthesis and assembly techniques that have been and are being employed in the fabrication of nano structured materials. One can find appropriate references in the literature recommended for further reading. Here only the main techniques for nanoparticles and nanomaterials fabrication are briefly considered . Identification of the emerging commonalities rather than the difference among different approaches are done. Methods for the synthesis of nanoparticles can be divided into three main groups.

1. Synthesis of semiconductor nanoparticles in solutions of the corresponding salts by controlled addition of anions (or cations) or by hydrolysis.
2. Preparation of nanoparticles as a result of phase transformations.
3. The synthesis of nanoparticles in aerosol.

The radiation-chemical method for the synthesis of nanoparticles is also known. Methods for the synthesis of complex multicomponent nanoparticles have been developed. Most of the semiconductor colloidal systems studied to date have been obtained by synthesizing the semiconductor nanoparticles in homogeneous solution. Commercial colloidal solutions containing the SnO_2 nanoparticles (with an average diameter of 3 nm) are available from Johnson Matthey (USA). Another commercially available nanoparticle is Degussa P_{25} TiO_2 powder containing 80% of anatase and 20% of rutile.

Synthesis of Semiconductor Nanoparticles in

Colloidal Solutions

The semiconductor nanoparticles could be prepared by chemical synthesis in homogeneous solutions, in different surfactant assemblies like micelles, vesicles, and Langmuir- Blodgett films, in polymers, glasses, zeolites, and β-cyclodextrin. The easiest and most common method for the preparation of semiconductor nanoparticles is the synthesis from the starting reagents in solution by arresting the reaction at a definite moment of time. This is the so-called method of arrested precipitation. Nanoparticles of metal sulfides are usually synthesized by a reaction of a watersoluble metal salt and H_2S or Na_2S in the presence of an appropriate stabilizer such as sodium metaphosphate. For example, the CdS nanoparticles can be synthesised by mixing $Cd(ClO_4)_2$ and Na_2S solutions:

$$\mathbf{Cd(ClO_4)_2 + Na_2S = CdS\downarrow + 2NaClO_4} \qquad \text{........1}$$

The growth of the CdS nanoparticles in the course of reaction is arrested by an abrupt increase in pH of the solution. Colloidal particles of metal oxides can be obtained by hydrolysis of the corresponding salts. For example, the TiO_2 nanoparticles are readily formed in the hydrolysis of titanium tetrachloride

$$\mathbf{TiCl_4 + 2H_2O = TiO_2\downarrow + 4HCl} \qquad \text{……2}$$

Formation of TiO_2 nanoparticles via reaction 2 is shown schematically in Figure2.

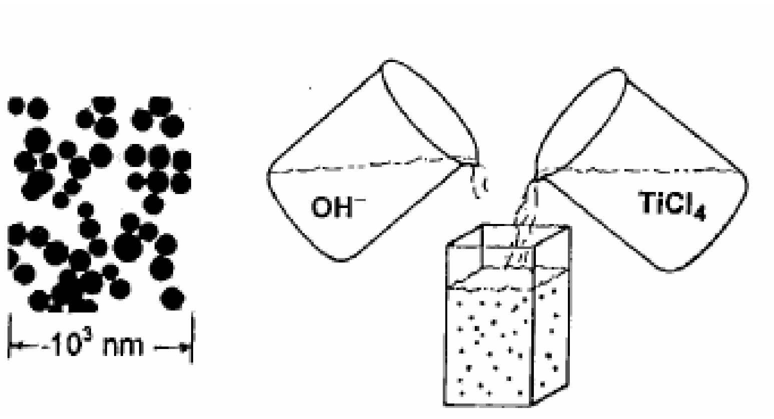
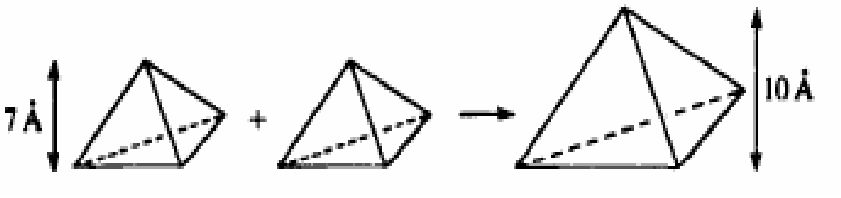


Figure 11. Scheme of TiO_2 nanoparticles formation by the method of arrested precipitation. TEM picture of TiO_2 nanoparticles is shown on the left.

Unfortunately, most of the colloidal solutions of nanoparticles; have low stability towards coagulation and possess a large size dispersion. Coagulation can be prevented by passivation of the surface of nanoparticles by hydroxyl ions, amines, or ammonia. Yet another procedure for the stabilization of colloidal solutions of nanoparticles is the coating of their surfaces with polyphosphates or thiols. As a result, one can obtain a stable colloidal solution of nanoparticles, isolate the nanoparticles as a powder, and then prepare a colloidal solution again by dispersing the powder in a solvent. Usually, the method of arrested precipitation results in a nonuniform size distribution of nanoparticles. It is possible to decrease the width of this distribution by monitoring the synthetic procedures and using high-pressure liquid chromatography and capillary electrophoresis. In the latter case, the separation of nanoparticles is achieved due to the different charge/size ratios for nanoparticles of different sizes. Small monodisperse semiconductor clusters (like e.g. Cd_4S_4) can be obtained by performing the synthesis inside zeolite cages. Larger semiconductor nanoparticles of fixed size could be synthesized by introducing additional molecules to a small initial cluster stabilized by organic ligands in a colloidal solution. For instance, it was found that the size of CdS clusters coated with thiophenolate ions can be increased if a metal sulfide is added to the solution. Such a polymerization of inorganic compounds appeared to be applicable to the synthesis of large semiconductor clusters of strictly fixed size from small particles like $[Cd_{20}S_{13}(SC_6H_5)_{22}]^{8-}$ clusters containing 55 cadmium and sulfur atoms from the pyramidal $[Cd_{10}S_4(SC_6H_5)16]^{4-}$ clusters containing 30 cadmium and sulfur atoms. The introduction of additional five sulfide ions leads to the fusion of two small clusters into one larger cluster. The process of the formation of a large cluster from two small ones can be illustrated by the following scheme:



The pyramidal structure of the $[Cd_{20}S_{13}(SC_6H_5)_{22}]^{8-}$ clusters was confirmed by X-ray analysis. Further addition of sulfide ions made it possible to obtain the $Cd_{32}S_{14}(SC_6H_5)_{36}$ tetrahedral clusters containing 82 cadmium and sulfur atons.

Usually, it is assumed that the nanoparticles containing several hundreds of atoms have a spherical or ellipsoidal shape. However, recent investigations have shown that the nanoparticles often have clearly defined facets and their shape is analogous to that of macroscopic crystals. The shape and size of nanoparticles is determined by electron microscopy. For a rough estimation of the size of nanoparticles, it is also possible to use the optical spectra of colloidal solutions. These estimates are based on the dependence of the position of the excitonic band of nanoparticles on their size, this dependence has already been discussed.

Dispersion of Macroscopic Particles in Solutions

It is possible to obtain semiconductor nanoparticles by sonication of colloidal solutions of large particles. Nanoparticles of layered semiconductors are also formed upon mere dissolution of large particles in an appropriate solvent, which was observed for MoS_2 and WS_2. Layered MoS_2-type semiconductors are characterized by a weak Vander Waals interaction between separate S - Mo - S layers. In the course of dissolution, the solvent molecules penetrate between the layers of the semiconductor and destroy large particles. In the case of MoS_2, the process of destruction can proceed until the formation of a two-layer particle. No further splitting of the semiconductor crystal occurs, since the formation of single-layer particles is accompanied by a considerable increase in the free energy of the system. Nanocrystals of layered PbI_2-type semiconductors have a disk-like shape and discrete “magic” sizes of the disks. For these semiconductors, a stable nanoparticle of a minimum size is assumed to be the smallest crystallite conserving the hexagonal symmetry of the macroscopic crystal. Such a crystallite is composed of two seven-atom iodine layers and two lead layers. Large stable nanoparticles are obtained from this 'seed' by the layer-by layer addition of extra iodide 'caps' symmetrically around the perimeter. An analogous structure is also assumed for MoS_2 nano particles.

Gas-Phase Synthesis of Nanoparticles

The gas-phase synthesis could also be used to get nanoparticles. Thus the Si nanoparticles are formed in 67% yield in the combustion of SiH_4 under oxygen-deficient conditions as a result of thermolysis of SiH4. Another method for the gas-phase synthesis of nanoparticles of various materials is based on the pulsed laser vaporization of metals in a chamber filled with a known amount of a reagent gas followed by controlled condensation of nanoparticles onto the support. A schematic view of the installation for the synthesis of nanoparticles is given in Figure 3. As the metal atoms diffuse from the target to the support, they interact with the gas to form the desired compound (for instance, oxide in the case of oxygen, nitride for nitrogen or ammonia, carbide for methane, etc.).

The pulsed laser vaporization of metals in the chamber makes possible to prepare nanoparticles of mixed molecular composition, such as mixed oxides/nitrides and carbides/nitrides or mixtures of oxides of different metals. Along with the reagent gas, the chamber contains an inert gas, such as He or Ar, at a pressure of 10-21 Torr, which favors the establishment of steady convection between the heated bottom plate and cooled top plate. In an experiment with a single pulse of a Nd:YAG laser (532 nm, 15-30mJ/pulse, 10-9 s pulse duration), over 1014 metal atoms are vaporized.

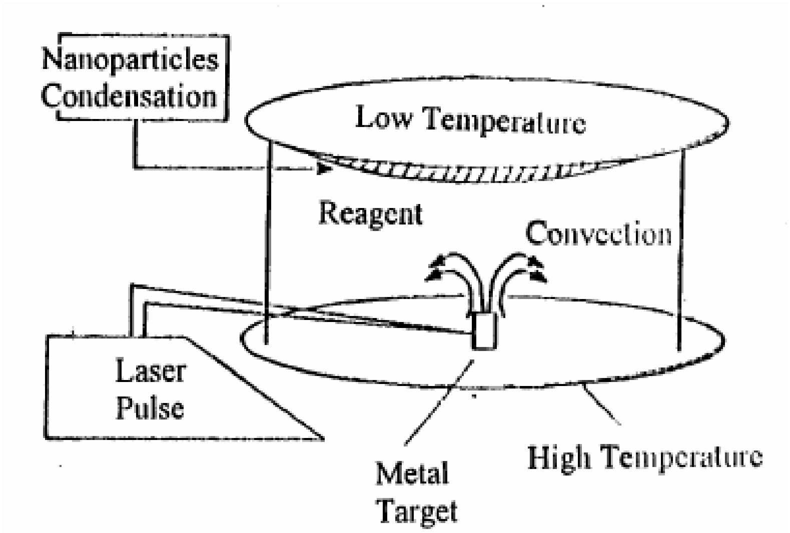


Figure 12. Schematic view of the installation for the synthesis of nanoparticles by laser vapourisation of metals.

A new compound is formed due to the reaction between the 'hot' metal atoms and the gas molecules, which is accompanied by the energy loss of the molecules formed by collisions with the inert gas atoms. The metal atoms that did not enter into reaction and the molecules of the new compound are carried by convection to the nucleation zone on the cooled top plate. By changing the composition of the inert gas and the reagent gas in the chamber and varying the temperature gradient and laser pulse power, it is possible to control the elemental composition and size of nanoparticles that are obtained.

Means to Achieve Monodispersity

One of the most challenging problems in synthesis is the controlled generation of monodispersed nanoparticles with size variance so small that size selection by centrifugal precipitation or mobility classification is not necessary. Among all the synthesis techniques discussed above, gas-phase synthesis is one of the best techniques with respect to size monodispersity. In this method, monodispersity is typically achieved by using a combination of rigorous control of nucleation/ condensation growth and avoidance of coagulation by diffusion and turbulence as well as by the effective collection of nanoparticles and their handling afterwards. The stability of the collected nanoparticle powders against agglomeration, sintering, and compositional changes can be ensured by collecting the nanoparticles in liquid suspension. For semiconductor particles, stabilization of the liquid suspension has been demonstrated by the addition of polar solvent. Surfactant molecules could be used to stabilize the liquid suspension of metallic nanoparticles.

Very monodispersed gold colloidal nanoparticies with diameters of about I nm could be prepared by reduction of metallic salt with UV irradiation in the presence of dendrimers. Poly (amidoamine) dendrimers with surface amino groups of higher generations have spherical 3-D structures, which may have an effective protective action for the formation of gold nanoparticles. Although the specific role of dendrimers for the formation of monodispersed nanoparticles has yet to be defined, good monodispersity is thought to come from the complex reaction accompanying the decomposition of dendrimers, which eventually leads to the conversion of solution ions to gold nanoparticles.

Synthesis of Nanoparticles of Mixed Composition

The high efficiency of recombination of the light-generated electrons and holes presents obstacles to the practical application of the semiconductor nanoparticles in photocatalysis. In this connection, the semiconductor nanocrystal hetero-structures composed of semiconductors with different structures of the electronic levels are of considerable interest.

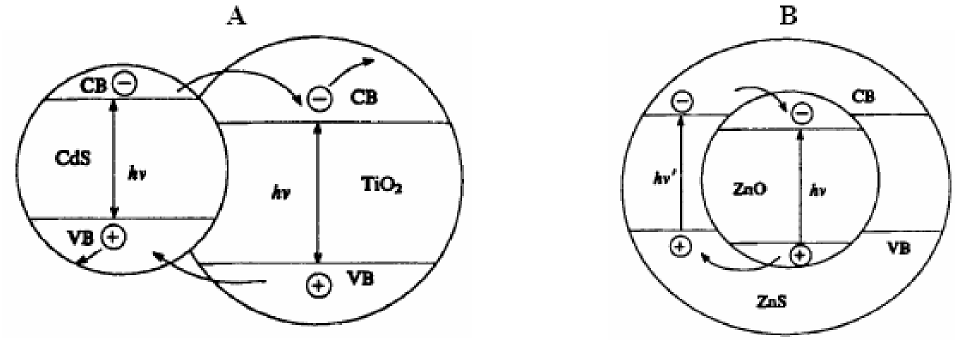


Figure 13. Schematic view of hetero-nanoparticies of different structure. CB stands for conduction band; VB stands for valence band.

With these structures, it is possible to attain high quantum yields of charge separation. The nanoparticles schematically shown in Figure 4 belong to this class of hetero-structures. The structures analogous to that shown in Figure 4A are known for CdS/TiO_2, CdS/ZnO, CdS/AgI, CdS/HgS, Cd_3P_2/TiO_2, Cd_3P_2/ZnO, and AgI/Ag_2S. For CdS/TiO_2, photoexcitation into the absorption band of US results in the electron transfer from CdS to TiO_2, while the hole remains in CdS. These structures are also of interest as nanoscale rectifier units for molecular electronics.

The formation of hetero-structures of the 'core-shell' type (see Figure 4B) has been demonstrated using the CdSe/ZnS and ZnS/CdSe nanoparticles as an example. These nanoparticles are obtained by controlled precipitation of semiconductor molecules of one type ('shell') on the pre-synthesized nanoparticles of another type ('core'). The synthesis of the shell is carried out in colloidal solution by methods analogous to those for the synthesis of one-component nanoparticles, considered above. The crystalline shells grow on the nanocrystal core despite the fact that the lattice constants in CdSe and in ZnS differ by 13%. The following 'core-shell' type nanoparticles have also been synthesised:

HgS/CdS,63 ZnS/ZnO and ZnO/ZnSe,68,69 $Ti0_2/Si0_2$ and $Ti0_2/SnO_2$,70 and $Ti0_2$/ZnO.71 These hetero-nanoparticles can, in turn, be coated with a layer of one more semiconductor. These types of nanocrystals have higher stability of electrons and holes and are interesting for photocatalysis.

Preparation of Nanostructured Semiconductor Films

Thin films of semiconductor nanoparticles are of considerable practical interest. Synthesis of these films is carried out by precipitation of pre-formed nanoparticles from colloidal solutions onto the supports, by direct precipitation of semiconductor molecules onto the support, and by oxidative hydrolysis of the corresponding metal salts at the anode. Usually, the films are 0.1 -1 μm thick. The following films of semiconductor nanoparticles are known: SnO_2, ZnO, TiO_2, WO_3, and Fe_2O_3. The SnO_2, ZnO, TiO_2, and WO_3 films were obtained by precipitation of nanoparticles. Direct precipitation of semiconductor molecules onto the support is used to prepare films of nanoparticles of semiconductors on the basis of Group II-VI elements. Oxidative hydrolysis of TiCl3 at pH 2.3 and a platinum anode potential of 0 V vs. saturated calomel electrode results in the formation of nanoparticles with an average diameter of 1-2 nm on the anode surface.

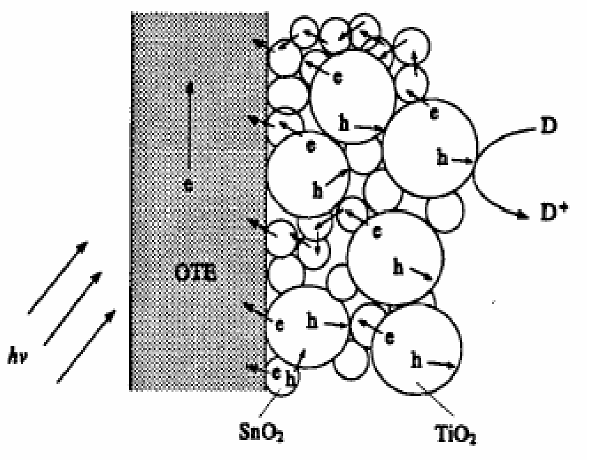


Figure 5. Schematic view of the process of photostimulated charge separation in the nanostructured Film composed of TiO_2 and SnO_2 nanoparticles adsorbed on an optically transparent electrode (OTE).

Nanostructured films containing nanoparticles of different semiconductors can be prepared by co-precipitation. A schematic view of such a film supported by the optically transparent electrode is given in Figure 5. Yet another method for the preparation of such films consists in wetting of a plate coated with a film of a certain type of nanoparticles with a solution containing metal ions followed by wetting of the plate with a solution containing sulfide ions. This procedure was used for the synthesis of films containing ZnO and CdS nanoparticies.

Building Nanoparticle Wires and Nanometer Fibers

As we have already discussed, recent paradigm shift envisioned for optoelectronics and computational devices involves the assembly of molecular or quantum wires. Chain aggregates of nanoparticles can be considered as polymer like units with their primary particles composed of a few hundred to a few thousand molecules. Depending on the particle size and its compositional material, the bonding force responsible for holding the aggregates together varies from weak van der Waals force for micrometer particles to strong chemical bonds for nanometer particles. The mechanical, optical, and electronic transport properties of these wires can be varied by controlling the diameter and the monodispersity of the primary particles, the crystalline structure, aggregate length, interfacial properties, and material purity. These chain aggregates can be formed by allowing agglomeration of nanoparticles generated by any of the synthesis techniques discussed above Recent advances in the fabrication of nanometer fibers or tubes offer another form of building blocks for nanostructured materials. An effective way to generate nanometer fibers (or tubes) is based on the use of membrane-template techniques. Membranes, with nanochannels generated by fission-fragment tracks or by electrochemical etching of aluminum metal, are used as templates for either chemical or electrochemical deposition of conductive polymers, metals, and semiconductors for the generation of nanofibers or tubes (C. R. Martin *Science*, **266**, 1961, 1994). Since the nanochannels on membranes are very uniform in size, the diameter and the aspect ratio of the nanofibers (or tubes) synthesized by the membrane template technique can be precisely controlled. Single crystal semiconductor nanofibers can also be grown catalytically by metalorganic vapor phase epitaxy and laser ablation vapor-liquid-solid techniques (A. M. Morales and C. M. Lieber, *Science*, **279**, 208 1998). These methods allow to synthesize one dimensional structures with diameters in the range of 3 to 15 nm. The advent of carbon-based nanotubes has created yet another way to fabricate nanometer fibers and tubes. These nanotubes have been used as templates for the fabrication of carbide and oxide nanotubes (T. Kasuga et al. *Langmuir*, **14**, 3160, 1998). The carbon nanotubes can now be catalytically produced in large quantities and have been used for reinforcement of nanostructural composite materials and concrete (A.Peigney et al. *Key Eng. Mat.* **132-136**, 743, 1997).

Carbon Nanotubes

Carbon nanotubes are unique nanostructures with remarkable electronic and mechanical properties. Interest from the research community first focused on their exotic electronic properties, since nanotubes can be considered as prototypes for a one dimensional quantum wire. As other useful properties have been discovered, particularly strength, interest has grown in potential applications. Carbon nanotubes could be used, for example, in nanometer-sized electronics or to strengthen polymer materials An ideal nanotube can be thought of as a hexagonal network of carbon atoms that has been rolled up to make a seamless cylinder. Just a nanometer across, the cylinder can be tens of microns long, and each end is "capped" with half of a fullerene molecule. Single-wall nanotubes can be thought of as the fundamental cylindrical structure, and these form the building blocks of both multi-wall nanotubes and the ordered arrays of single-wall nanotubes called ropes. Figure 15 shows an image of a fragment of a one-wall carbon nanotube.

The nanotubes could be prepared by the laser vaporization of a carbon target in a furnace at 1200 °C. A cobalt-nickel catalyst helps the growth of the nanotubes, presumably because it prevents the ends from being "capped" during synthesis, and about 70-90% of the carbon target can be converted to single-wall nanotubes. By using two laser pulses 50 ns apart, growth conditions can be maintained over a larger volume and for a longer time. This scheme provides more uniform vaporization and better control of the growth conditions.

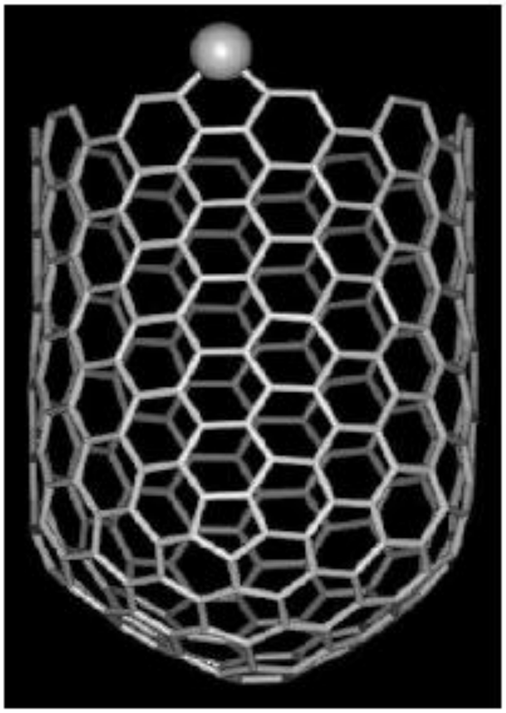


Figure 15. A fragment of a one-wall carbon nanotube.

Flowing argon gas sweeps the nanotubes from the furnace to a water-cooled copper collector just outside of the furnace.

A carbon-arc method has been developed to grow similar arrays of single-wall nanotubes. In this case, ordered nanotubes were also produced from an ionized carbon plasma, and joule heating from the discharge generated the plasma. In a scanning electron microscope, the nanotube material produced by either of these methods looks like a mat of carbon ropes. The ropes are between 10 and 20 nm across and up to100 μm long. When examined in a transmission electron microscope, each rope is found to consist of a bundle of single-wall carbon nanotubes aligned along a single direction.

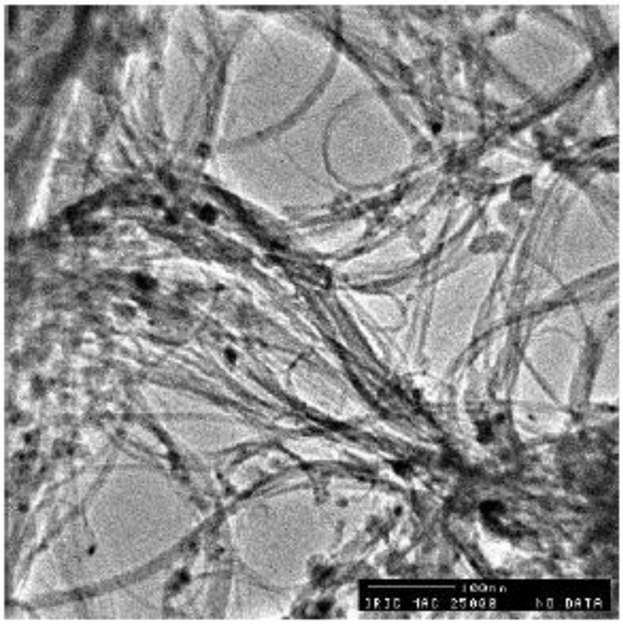


Figure 16. SEM image of the nanotube material produced by the laser vaporization of a carbon target.

X-ray diffraction, which views many ropes at once, also shows that the diameters of the single-wall nanotubes have a narrow distribution with a strong peak. While multi-wall carbon nanotubes do not need a catalyst for growth, single-wall nanotubes can only be grown with a catalyst. However, the detailed mechanisms responsible for growth are not yet well understood.

Experiments show that the width and peak of the diameter distribution depends on the composition of the catalyst, the growth temperature and various other growth conditions. Great efforts are now being made to produce narrower diameter distributions with different mean diameters, and to gain better control of the growth process. From an applications point of view, the emphasis will be on methods that produce high yields of nanotubes at low cost, and some sort of continuous process will probably be needed to grow carbon nanotubes on a commercial scale.

Langmuir-Blodgett Films

Following the realization of Lord Rayleigh that a film of oil on water was just one molecule thick Langmuir demonstrated that monolayers of fatty acids could be ordered on the surface of water by application of pressure undergoing phase changes from a gaseous state of non-interacting molecules to a "solid" state where the molecules interacted in a rigid film. Langmuir and Blodgett realized the transfer of such monolayers from the water surface to a solid substrate by slowly passing an appropriately treated substrate through the air/water interface. Figure 17 schematically shows the deposition of Langmuir-Blodgett film from a floating Langmuir monolayer.

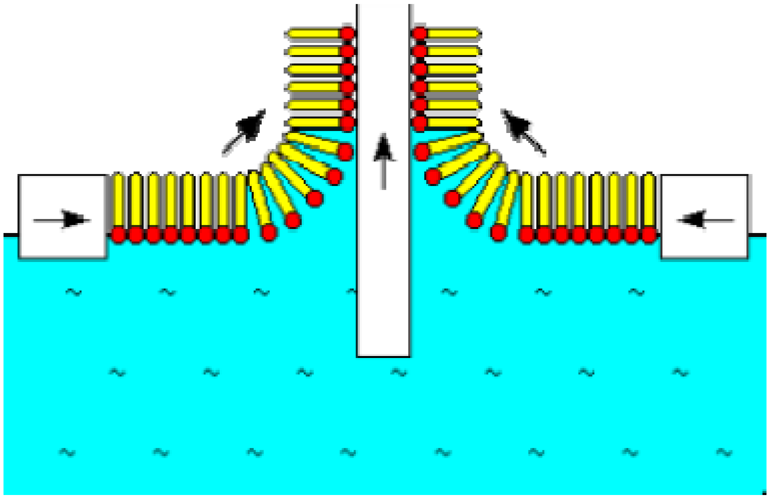


Figure 17. Deposition of Langmuir-Blodgett film from a floating Langmuir monolayer

In practice films are spread on an ultra clean water sub phase in a teflon trough in a clean room (class 100). The trough has a moveable teflon barrier straddling the air water interface and this is controlled mechanically to compress the film under servocontrol. As the surface area of the film is thus reduced the surface pressure of the film increases. The pressure-area isotherm is monitored continuously and at some area/molecule the pressure will begin a rapid increase as the solid phase is reached while the area per molecule remains approximately constant. If the pressure increases much further the film will be liable to collapse.

At some predetermined pressure in the solid phase the film pressure is held steady. A substrate may now be passed through the air/water interface and as monolayers are picked up the film area will reduce. The pressure is held constant by feedback from a pressure monitor and the reduction of area is monitored to find a transfer ratio, (area of slide covered)/(loss of area from film on trough). Ideally this should be 100% but it may be greater (if for example the molecules are slowly dissolving into the sub phase) or less if incomplete coverage of the slide is achieved. If the first is occurring this should be noticed by monitoring the area of the film for some time before attempting to transfer a monolayer. If the area is gradually reducing this would suggest that the molecules are either dissolving into the sub phase or leaking under the barrier.

Many factors may influence film-forming characteristics some of which are:

- temperature of subphase
- pH of subphase
- purity of subphase
- addition of ions to stabilize films.

Fatty acid molecules are amphiphilic with a long aliphatic chain that is hydrophobic preventing dissolution of the molecule and a carboxylic acid head group, which is hydrophilic attaching itself to the water surface. Many molecules with this arrangement of hydrophilic and hydrophobic moieties will for Langmuir Blodgett films. By attaching such parts to an electro or optically active molecule a functionalised molecule may be made. Because the films are vector ordered when transferred to the substrate multilayers with desired electro/optical properties may be assembled.

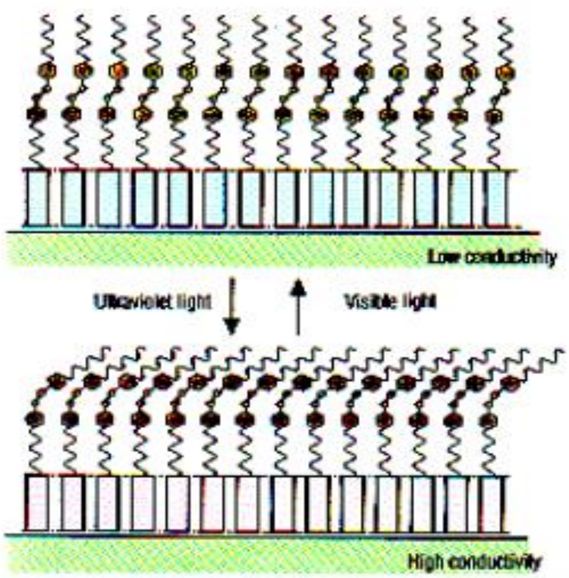


Figure 18. The conductivity of LB film can be switched by the irradiation of light.

Langmuir-Blodgett (LB) films, constructed by transferring monolayers floating on water surface to a solid substrate, are expected to be widely applied to molecular electronic and bioelectronic devices because of characteristics such as the thickness and molecular arrangement being controllable at the molecular level. As an example, Figure 18 shows

Langmuir-Blodgett film that has different conductivity upon illuminating by the light. Illumination of the fatty acid molecules presented in this figure changes the molecular conformation from *cis* to *trans* (visible light) or from *trans* to *cis* (UV light) thus changing the electrical conductivity of the molecule.

Biogenic Strategies

The ability of amphiphilic molecules to self organize in aqueous solutions could be used to produce nanomaterials in which self-assembled organic materials are used as templates or scaffolding for inorganic components. As one example of such self assembled or self-organized materials, Mc. Gehee et al. (Synthesis of mesoscopic structures by co-

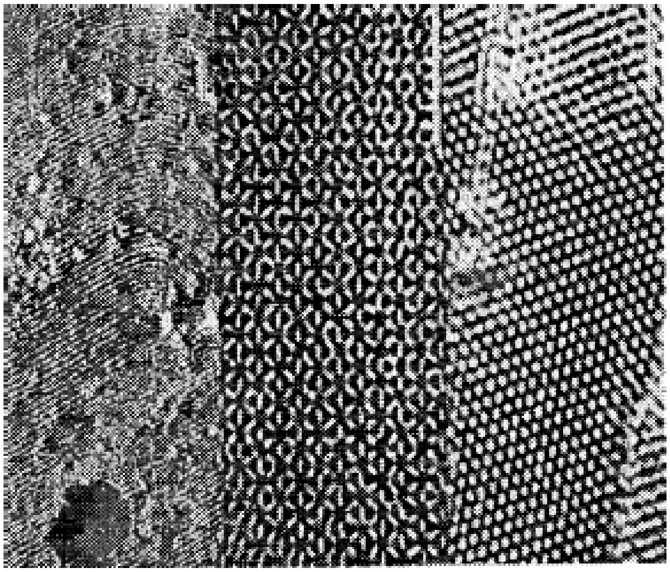


Figure 19. TEM images of (a) the lamellar morphology, (b) the cubic phase, And (c) the hexagonal phase of the silica//surfactant nanostructured composites by co- assembly. The whole size of the picture is 300×300 nm2. (McGehee et al. Synthesis of mesoscopic structures by co- assembly, In *Proc. 52nd Annual Mtg. MSA,* San Francisco, 1994)

assembly, In *Proc. 52nd Annual Mtg. MSA*, San Francisco, 1994) have mixed silica precursors with surfactants that have self-ordered to form various surfactant water liquid crystals. A range of various structures built from walls of amorphous silica was observed (see Figure 19).

These structures are organized about a repetitive arrangement of pores up to a hundred angstroms in diameter. This example shows that the

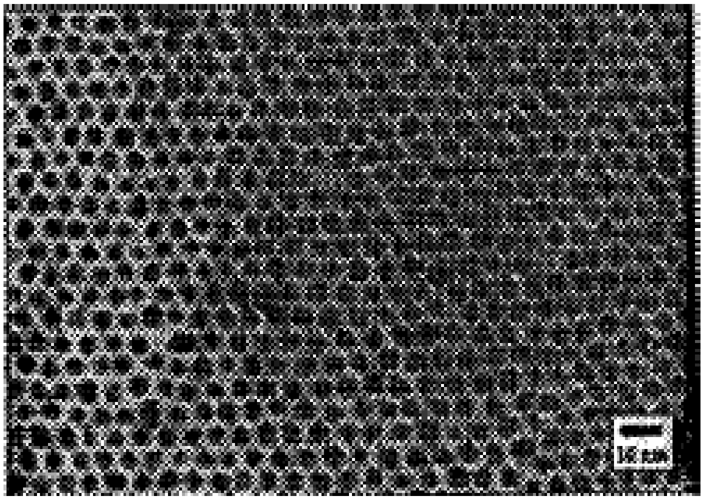


Figure 20. TEM image of unlinked cluster array of 3.7 nm Au nanoparticles encapsulated by dodecanethiol. (Andres et al. The design, fabrication and electronic properties of self-assembled molecular nanostructures.

(Andres et al. The design, fabrication and electronic properties of self-assembled molecular nanostructures. In *The handbook of nanostructured materials and nanotechnology*, ed. H. S. Nalwa, San Diego, Academic Press, 1998).

addition of organic molecules can strongly influence the resulting structure of inorganic components. Such strategies have been adopted in synthetic formation of nanostructures, such as in the formation of networks of gold clusters Another example of self-organized nanomaterials is shown in Figure

20. Gold clusters 3.7 nm in diameter, formed in the vapor phase, could be encapsulated in organic surfactants, such as dodecanethiol, forming a colloidal suspension. The surfactants prevent the agglomeration of the gold clusters. Addition of small amount of dithiol precipitates out a 3-13 cluster network, which can in turn be deposited onto another solid substrate. Figure 20 shows a transmission electron microscope image of a cluster array spin-cast onto MoS_2. The methodology of self-assembly has even been extended to physical vapor deposition processes where it would seem more difficult to control the nucleation and growth of three-dimensional nanostructures. Utilizing the strain inherent in the epitaxial growth of lattice-mismatched materials, and the expected strain-induced transition from two-dimensional

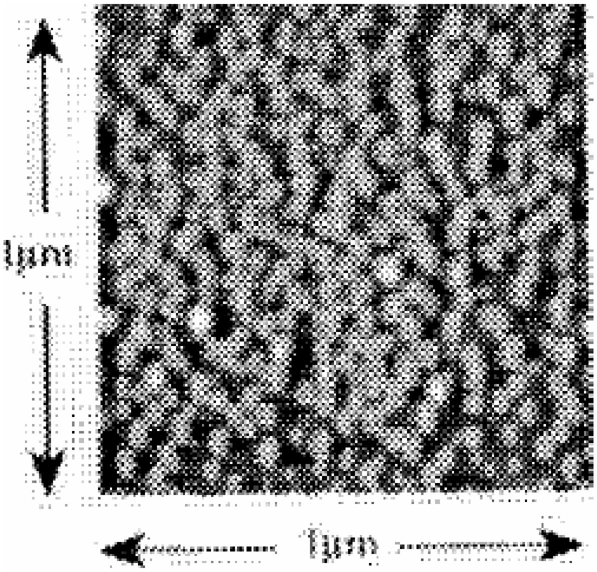


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Figure 21. Array of In As nanoparticles grown on GaAs substrates. (R. A. Mirin, et al. *Elect. Lett.* **32**, 1723-1734, 1996)

(layered) to three-dimensional (islanded) growth, researchers have been able to form arrays of semiconductor quantum dots (~20-30 nm in diameter, ~1011 cm-2 in density, a size variation of about ±7%) (Leonard et al. *Appl. Phys. Lett*. **63**, 3203-3205, 1993). An example of such "self-assembled" semiconductor quantum dots is shown in Figure 21.

The achievement of arrays of several billions of quantum dots of these dimensions with such a size variation is beyond the capability of standard high resolution lithographic and pattern transfer processes. Moreover, the controlled formation of critical surfaces and interfaces without the intercession of ion-assisted processing that can introduce potential defects into the materials has produced a rich source of optically and electronically efficient quantum structures. Such self-assembled dots have already incorporated into laser structures. Chemical specificity may provide the most robust means of ensuring control of size and placement of nanostructured building blocks. Recent work in the synthesis of compound semiconductor quantum dots from chemical precursors have provided even tighter distributions of size variation (±5 %) than those shown in the strain-induced selfassembled dots (J. E. B. Katari et al. *J. Phys. Chem*. **98**, 4109, 1994). The size-dependent and energy-selective optical absorption properties of such chemically synthesized quantum dots .

Heavy points of Organic Nanoparticles

- Easy to synthesized
- Easy to process
- Easy to deposit
- Just of Nanometric size

- Interesting optical/electrical Properties

Different types of Nanoparticles

- Metallic Nanoparticles
- Semiconducting Nanoparticles

Different Materials

- Au, Ag, CdSe, CdS, PbS, …

Different synthesis procedures

- Liquid Phase
- Solid Phase
- Within a Precursor Matrix

Gold Nano Particles

Nanoparticles in the 1-100 nm range can be said to bridge the gap between small molecules and bulk materials. Metal nanoparticles, especially gold, silver and copper nanoparticles, have been extensively investigated due to their unique electronic, optical and catalytic properties.

These properties are neither those of bulk metal nor those of molecular compounds as have been widely demonstrated in both experimental and theoretical investigations, but they strongly depend on the particle size, shape of the nanoparticles, and interparticle distance as well as the nature of the protecting organic shell.

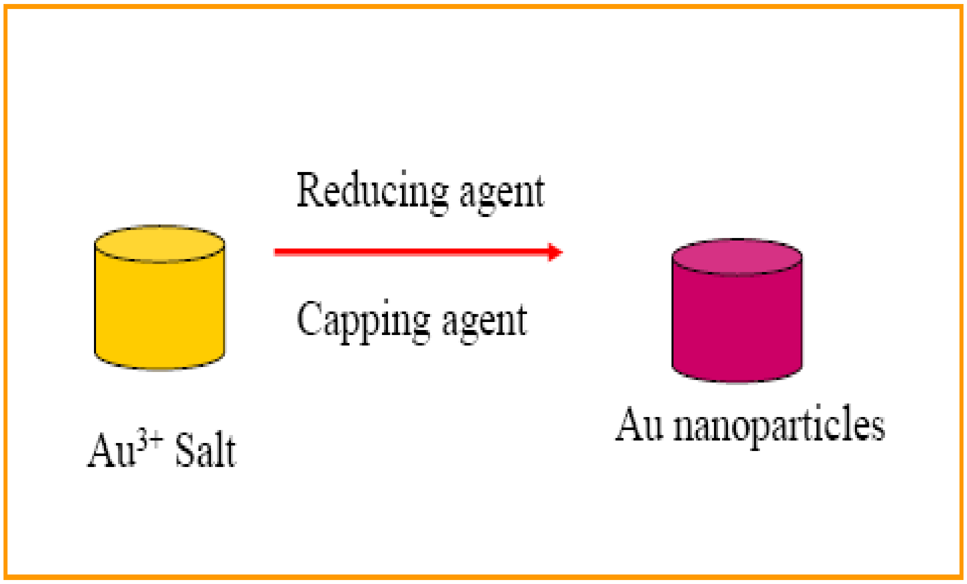
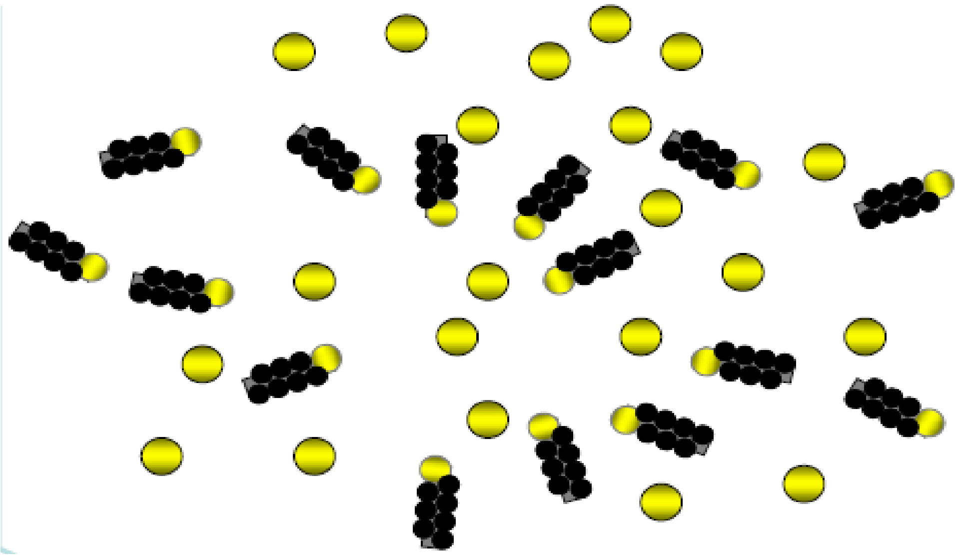


Fig.22. NANOPARTICLES by Liquid Phase
Preparation via a chemical route



23. GOLD NANOPARTICLES

GOLD NANOPARTICLES

Biphasic reduction procedure

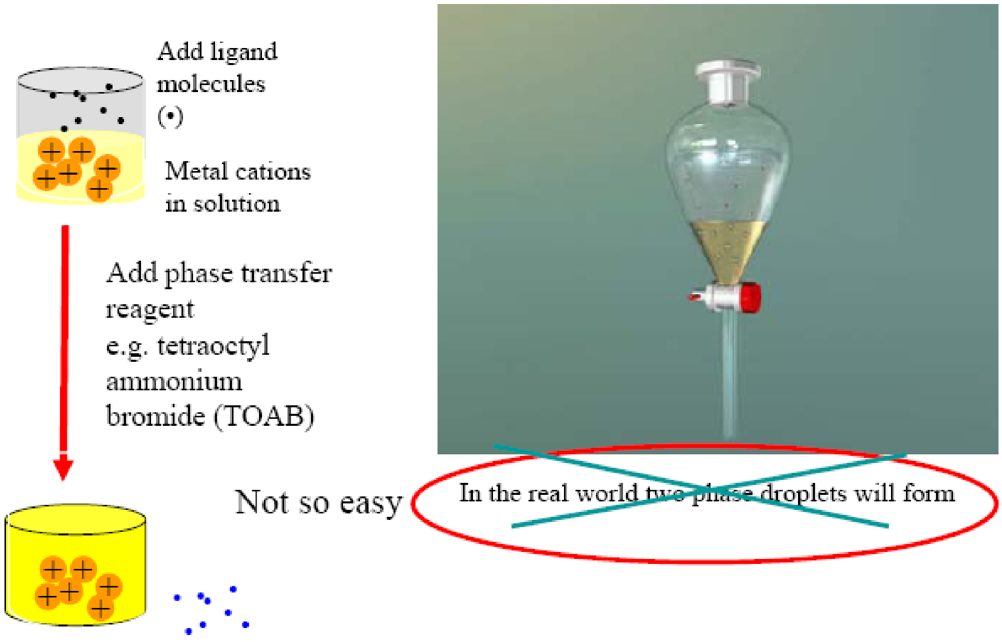


Fig24. Biphasic Reduction Procedure

Gold is the most stable noble metal at the nano-scale. Ligand protected gold nanoparticles offer a unique surface chemistry that allows it to be used as a platform on which to self-assemble layers of organic molecules, usually bound to the gold by carefully placed sulphur atoms. The synthesis of gold nanoparticles with chemically bound polymer grafts can be carried out in two ways, i.e., “grafting-to” and “grafting-from”. It is significant that both methods can be combined with controlled/living radical polymerization techniques, such as RAFT and ATRP, to obtain well-defined and highly dense polymeric shell surrounding the gold cores.

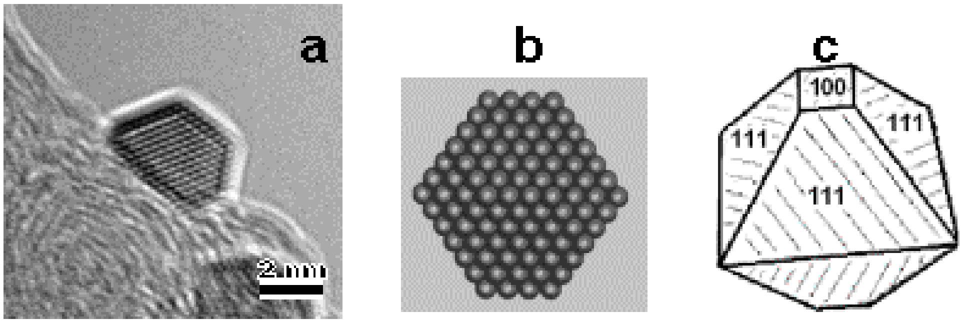


Fig. 25. Micrograph of polymer protected gold nanoparticles (a), the shape of gold nanoparticles--truncated octahedral (b) and (c).

In our lab, we have successfully prepared poly(N-isopropylacrylamide) protected gold nanoparticles and amphiphilic gold nanoparticles grafted either with both poly(N-isopropylacrylamide) and polystyrene homopolymers or their block copolymers, by using either/both of the two ways mentioned above.

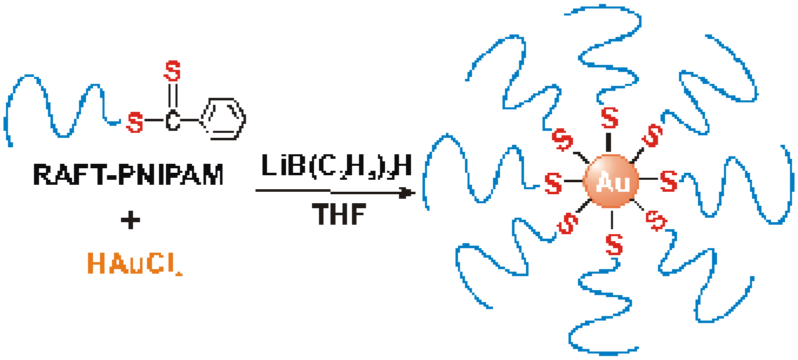


Fig. 26. Schematic representation of synthesis of PNIPAM-AuNPs using RAFT-PNIPAM by a “grafting-to” technique.

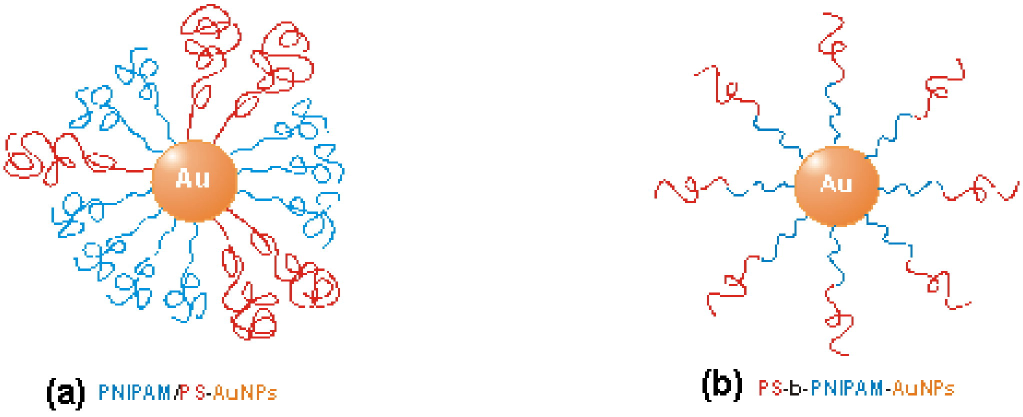


Fig. 27. The structures of gold nanoparticles grafted with both PNIPAM and PS homopolymers (a) and with PS-b-PNIPAM chains (b).

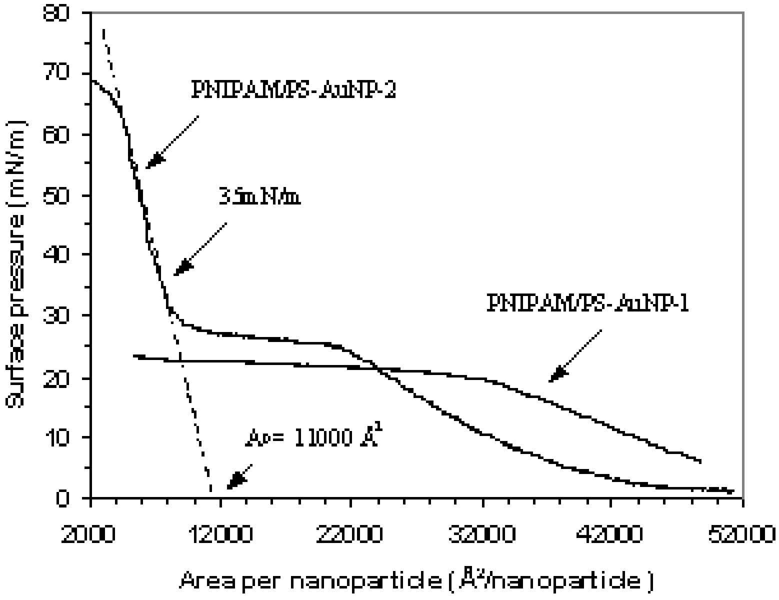


Fig. 28. Isotherms of the surface pressure versus area per gold nanoparticle for PNIPAM/PS-AuNP-1 and –2.

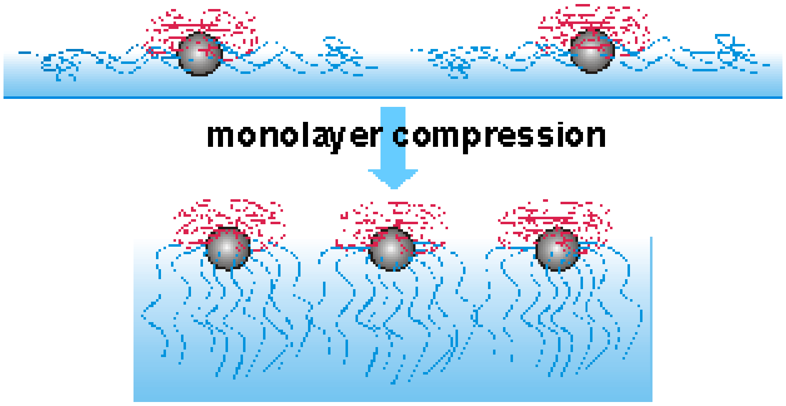


Fig. 29. Schematic representation of the conformational change of tethered PNIPAM chains from the flattened and stretched chains at the air-water surface to forming a brush-like structure in the water subphase with the monolayer compression.

Using these gold nanoparticles, we have studied i) the colloidal properties, ii) the surface isotherms of thermoresponsive Langmuir monolayers, iii) the particle assemblies in the deposited Langmuir-Blodgett films and at the air-water interface, iv) the optical properties of the particle assemblies.

****

IV.Novel Synthesis

and

Applications

of

Nanocrystals

IV. NOVEL SYNTHESIS AND APPLICATIONS OF NANOCRYSTALS*

(From Current Researches)

i) Nanocrystals of metals, semiconductors and oxides:

Films of nanocrystals such as Au, Ag and Pd, semiconducting sulphides such as CdS, ZnS and CoS, and oxides such as Fe2O3 and CuO have been prepared by employing reactions at liquid–liquid (organic–aqueous) interfaces. In this method, a suitable organic derivative of the metal taken in the organic layer reacts at the interface with the appropriate reagent present in the organic layer. Two typical applications of nanocrystals pertaining to magnetic devices and dip-pen lithography are briefly presented.

THE synthesis and characterization of nanocrystals of materials have become an area of intense research activity over the last few years1–11. Several methods have been reported for the preparation of nanocrystals of metals such as Au and Ag and of semi-conductors such as CdS and CdSe7–11. Thus, metal nanocrystals are generally obtained by the controlled reduction of metal salts, while nanocrystals of metal chalcogenides and oxides are prepared by arrested precipitation or thermal decomposition1– 6. Although much has been achieved in controlling the size distribution of nanocrystals, it has often been difficult to obtain robust films of nanocrystals through self-assembly. Producing nanocrystal films by molecular beam epitaxy and other physical methods often tends to be tedious and equipmentintensive. We have made use of the interface between two immiscible liquids to prepare nanocrystals of metals, semiconductors and metal oxides as well as thin films of these materials. In this method, the organic layer containing the metal precursor comes into contact with the aqueous layer containing a suitable reagent for reduction, hydrolysis or sulphidation. The reaction occurs at the interface, depositing the nanocrystals at the interface, the yield and the size distribution depending on the reaction parameters such as reagent concentration, mode of dispersal of reagents, mechanical agitation, temperature and viscosity of the medium. By an appropriate choice of the reaction parameters, we can obtain isolated nanocrystals with a narrow size distribution or well-formed films of the nanocrystals. It is noteworthy that the present method is distinct from the methods where a phase boundary is used to slow down diffusion to another medium7.

*Dedicated to Prof. S. Ramaseshan on his 80th birthday.

**For correspondence. (e-mail: cnrrao@jncasr.ac.in)

In this communication we briefly present typical results obtained by this method to illustrate its versatility. Nanocrystals of metals and semiconductors are finding a variety of applications starting from biological tagging to electronic devices. We present preliminary results of our study of g-Fe_2O_3 nanocrystalline films to explore anisotropic magnetization, and of aqueous dispersions of metal nanocrystals as inks in dip-pen lithography. In order to prepare nanocrystals of Au, the triphenyl phosphine derivative of the metal ($Au(PPh_3)Cl$) was dispersed in the toluene layer and the reducing agent, tetrakis-hydroxy-methylphosphonium

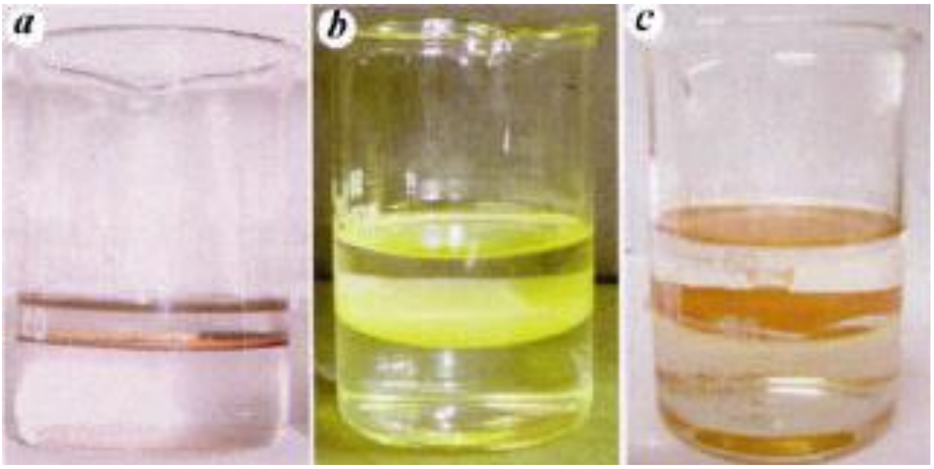


Figure 30. Nanocrystals of (***a***) Au, (***b***) CdS and (***c***) *g*-Fe2O3 formed at the toluene–water interface.

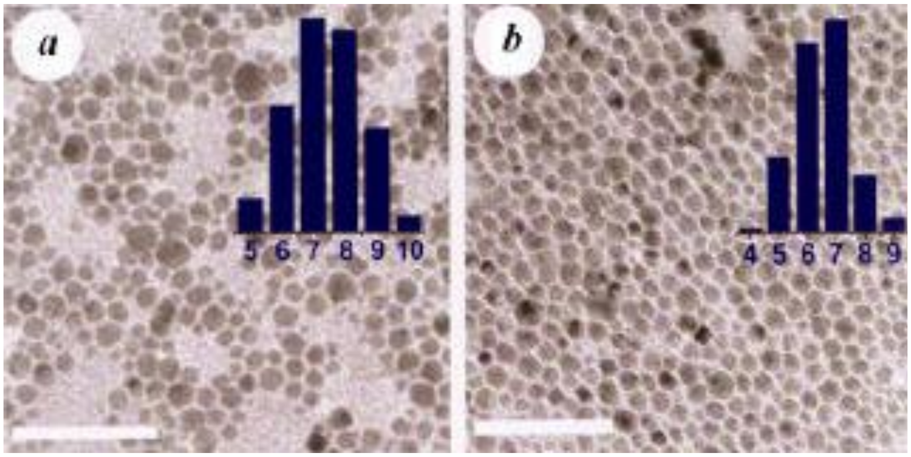


Figure 31, TEM image of the as-prepared Au nanocrystals obtained after 24 h from a liquid–liquid interface containing a 1.5 mM solution of Au(PPh_3)Cl in toluene and 330 ml of 50 mM THPC in 16 ml of 6.25 mM aqueous NaOH solution in a 50 ml beaker (bar = 50 nm). ***b***, TEM image of Au nanocrystals obtained starting with a 6 mM toluene solution of Au(PPh3)Cl and 1.65 ml of 50 mM THPC in 16 ml of 31.25 mM aqueous NaOH solution (bar = 50 nm). (Inset) Particle size distribution (in nm).

chloride11,12 was injected into the aqueous layer containing alkali. Figure 30 shows how the reaction carried out at 298 K was confined exclusively to the liquid–liquid interface. Examination of the films at the interface by transmission electron microscopy (TEM) revealed that they consisted of close-packed Au nanocrystals. In Figure 31, we show TEM images of the Au nanocrystals obtained with two different concentrations of $Au(PPh_3)Cl$.

We observe that with increase in the concentration of the metal precursor we get films of nanocrystals with more number of particles, but the size distribution is not greatly effected. Use of a low concentration of the metal precursor results in some metal nanoparticles in the aqueous layer below the film at the interface, while a high concentration of the metal precursor gives metal nanoparticles in the organic layer. We obtain films of metal nanoparticles only at the interface, leaving both the liquid layers clear, only when an optimal precursor concentration is employed.

The temperature of the reaction has a marked effect on the size distribution of the Au nanocrystals, as can be seen from the TEM images in Figure 32.

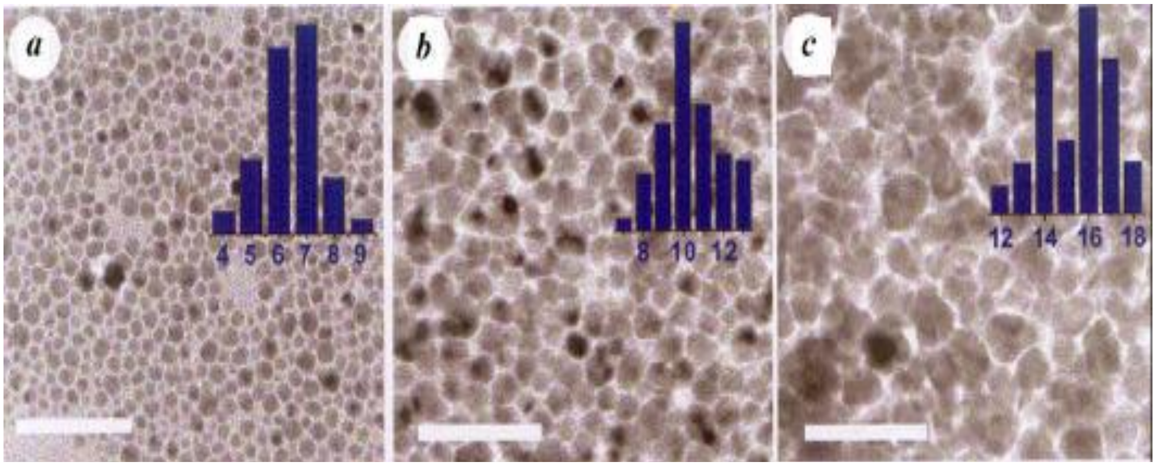


Figure 32, TEM image of Au nanocrystals obtained at room temperature from a liquid–liquid interface containing a 1.5 mM toluene solution of Au(PPh3)Cl and 330 ml of 50 mM THPC in 16 ml of 6.25 mM aqueous NaOH solution in a 50 ml beaker (bar = 50 nm). TEM image of (***b***) particles obtained at 323 K (bar = 50 nm) and (***c***) particles obtained at 348 K (bar = 50 nm). (Inset) Size distributions of the particles.

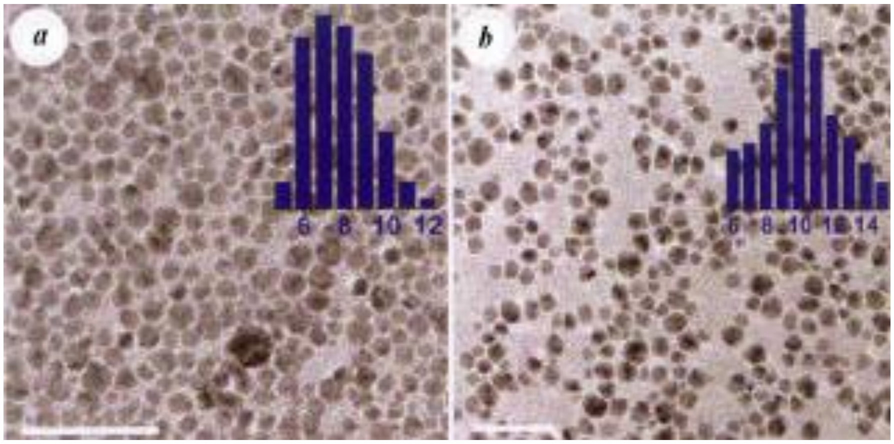


Figure 33. ***a***, TEM image of Au particles obtained at room temperature by reacting a THPC solution in a 3 : 1 water–glycerol mixture and Au(PPh3)Cl in toluene layer (bar = 50 nm). ***b***, TEM image of Au particles obtained at room temperature by reacting a THPC solution in a 1 : 1 water–glycerol mixture and Au(PPh3)Cl in toluene layer (bar = 50 nm). (Inset) Particle size distributions.

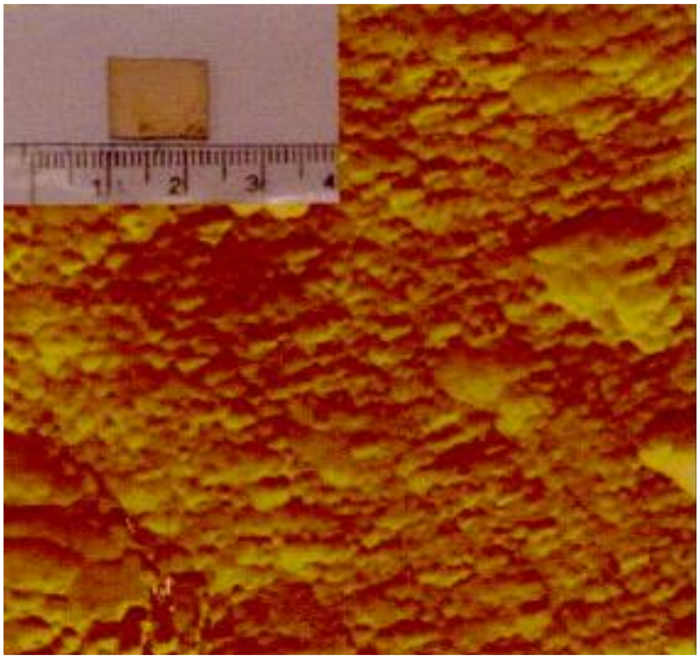


Figure 34. Tapping mode atomic force microscopic image (in phase contrast mode) of an Au film transferred to a highly oriented pyrolytic graphite substrate. The film was prepared starting with 10 mM solution of Au(PPh3)Cl in toluene. (Inset) Similar film on a glass substrate.

When the reaction is carried out at different temperatures in a hot-air oven, the average particle size varies from 7 nm at 298 K to 16 nm at 348 K. We have examined the effect of viscosity of the aqueous layer on

particle size distribution by adding glycerol to the aqueous layer. The particle size decreases significantly as the proportion of glycerol and the associated viscosity of the aqueous layer increases. TEM images in Figure 33 clearly demonstrate the effect of viscosity. By employing high concentration of metal precursors, lustrous thin films of gold of varying thickness could be prepared. The films are readily transferred to a solid substrate by raising the substrate gently across the interface. Preliminary cross-sectional scanning electron microscopic and atomic force microscopic (AFM) investigations reveal that the thickness of the films varies in the range of 80– 1000 nm on varying the concentration of the precursors. Tapping mode AFM studies show the presence of aggregates of granules in the films with a rms roughness of 35 nm (Figure 34).

An important feature of the liquid–liquid interface method is that the nanocrystals at the interface can be transferred to either the aqueous or the organic phase using appropriate capping agents. For example, by the addition of dodecanethiol to the organic layer, the Au nanocrystals could be transferred entirely to the organic layer, while the addition of mercaptoundecanoic acid transferred the nanocrystals to the aqueous layer. The transfer of the Au nanocrystals to the aqueous or the organic medium is marked by the acquisition of a vivid colour by the respective layer, as demonstrated in Figure 35.

There is little change in the average diameter of the nanocrystals after transfer to the organic or the aqueous medium from the interface. We have been able to obtain nanocrystals of other metals such as silver and palladium as well, by employing the liquid–liquid interface. In Figure 36, we show a TEM image of the small Pd nanocrystals obtained by reacting a dispersion of palladium acetate in the toluene layer with THPC in the aqueous layer.

We have attempted to characterize the metal nanocrystal films obtained at the interface by electrical-resistivity measurements. We observe different resistivity behaviours in the films prepared at different

Figure 35. (Middle) Nanocrystals of Au formed at the toluene–water interface. (Left) When dodecanethiol is added to the toluene layer, the Au nanocrystals form an organosol. (Right) When mercaptoundecanoic acid is added to the water layer, the Au nanocrystals produce a hydrosol.

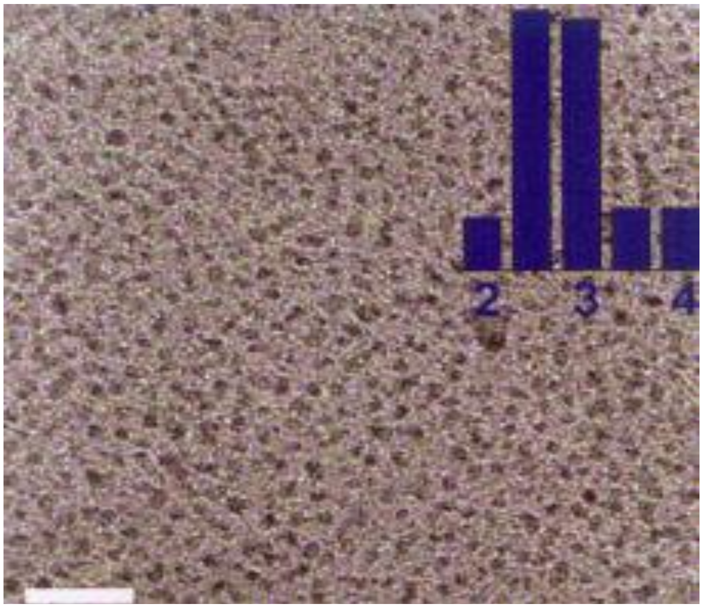


Figure 36. TEM image of Pd nanocrystals obtained at room temperature by reacting a 2.2 mM toluene dispersion of palladium acetate with 330 ml of 50 mM THPC in 16 ml of 6.25 mM aqueous NaOH solution in a 50 ml beaker (bar = 20 nm). (Inset) Particle size distribution.

temperatures and concentrations. For example, films of Au obtained at 298 K show a non-metallic behaviour of resistivity, while the ones prepared at 348 K exhibit metallic behaviour.

A study of the transport properties of the films prepared under different reaction conditions is currently in progress, in order to relate the structure of the film with the resistivity behaviour.The universality of the use of the liquid–liquid interface for the synthesis of nanocrystals is demonstrated by the successful synthesis of CdS and other metal sulphide nanocrystals. That the reaction occurs at the interface in these cases as well can be seen clearly from Figure 1 *b*. CdS nanocrystals with an average diameter of ~ 5 nm were obtained by reacting cadmium cupferronate in the toluene layer with Na2S in the water layer at 298 K (Figure *37a*).

The particles exhibit the blue-shifted absorption band at 450 nm (bulk value 515 nm). CdS nanocrystals of ~ 8 nm diameter were obtained by carrying out the reaction at 353 K. This method could be readily extended to prepare films of nanocrystalline CoS, NiS, CuS and ZnS. In Figure 37b, we show the TEM image of CoS nanocrystals obtained by reacting cobalt stearate in the toluene layer with Na2S in the aqueous layer. Nanocrystals of *g*-Fe2O3 with a diameter of ~ 2.6 nm were obtained by reacting iron cupferronate in the toluene layer with NaOH in the water layer (Figure 9 *a*). The *g*-Fe2O3 particles are superparamagnetic. ZnO nanocrystals and nanorod-like structures exhibiting a blue-shifted luminescence could be prepared starting with zinc cupferronate in the organic layer and NaOH in the aqueous layer.

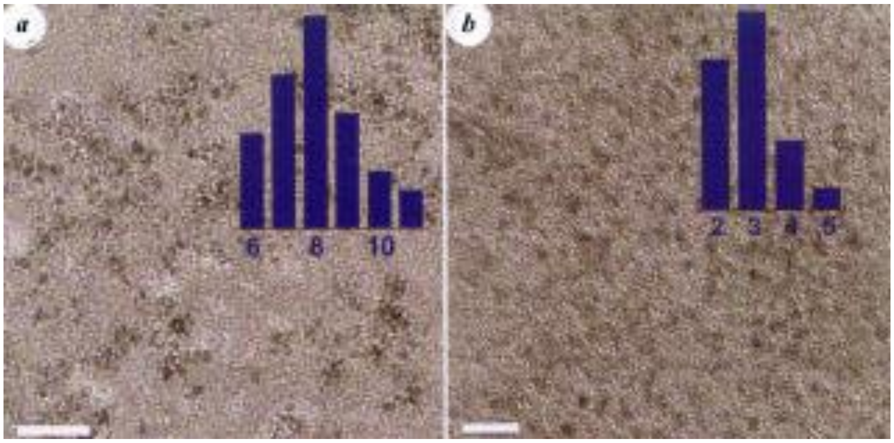


Figure 37. a, TEM image of CdS nanocrystals (~ 8 nm average diameter) prepared at the water–toluene interface. The sample was prepared by treating 0.05 mM solution of cadmium cupferronate in toluene with 0.10 mM aqueous Na2S for 12 h (bar = 50 nm). ***b***, TEM image of CoS nanocrystals (~ 3 nm average diameter) prepared at the water–toluene interface using the same concentration of starting materials as that of CoS (bar = 10 nm).

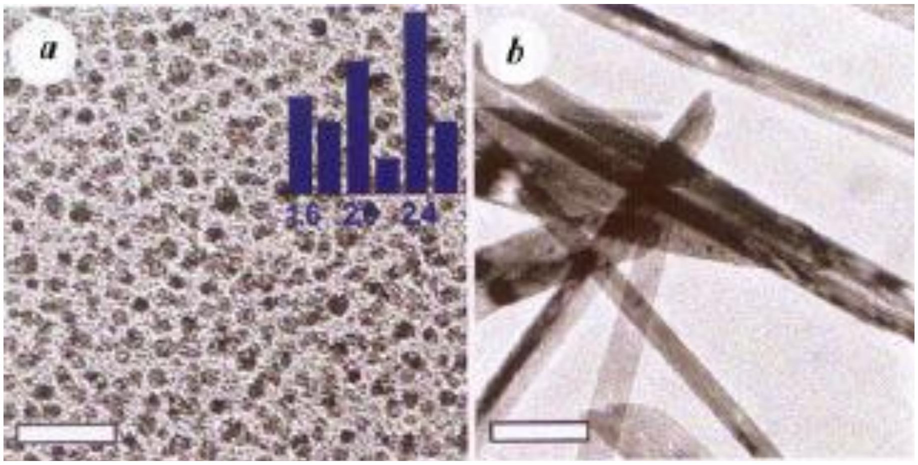


Figure 38,a, *g*-Fe2O3 nanocrystals (~ 2.6 nm average diameter) obtained from a interface film, starting with 0.0428 mM iron(III) cupferronate solution in toluene, allowing it to react with 1.87 mM aqueous NaOH for 8 h at room temperature. The nanocrystals are quite monodisperse in nature (bar = 10 nm). ***b***, CuO nanorods obtained by reacting a dispersion of 0.02 g of Cu(cup)2 in toluene with 20 ml 1N NaOH solution for 36 h (bar = 200 nm).

Similarly, using a dispersion of copper cupferronate in the toluene layer and with NaOH in the aqueous layer, nanorods of CuO have been obtained.Figure 38 *b* shows the TEM image of CuO nanorods. This method can clearly be extended to prepare other metal-oxide nnanocrystals as well. Films of *g*-Fe2O3 nanocrystals of various thicknesses were deposited on solid substrates by successive addition of dispersions of the nanocrystals in toluene or in water. Films of citrate-capped *g*-Fe2O3 prepared by us on Si(100) substrates were smooth, extending to several microns.

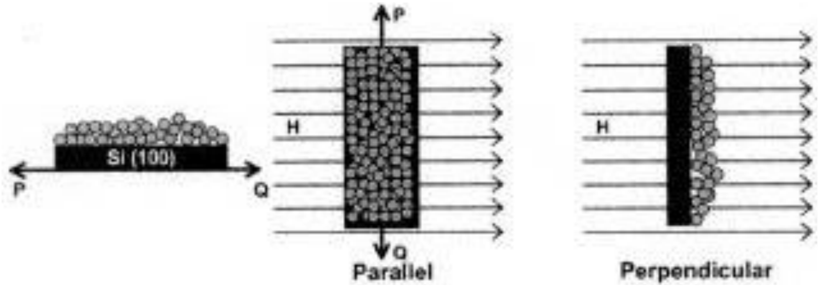


Figure 39. Schematic illustration of the two different orientations of *g*-Fe_2O_3 nanocrystalline films along which magnetic measurements were carried out. Change in the orientation was brought about by rotating the film along the *PQ* axis.

Tapping-mode AFM images reveal that the films are composed of ~ 12 nm diameter nanoparticles. The films were magnetic showing hysteresis, unlike the nanoparticles which were only superparamagnetic. Magnetic measurements were carried out along two different orientations of the film (Figure 39). Interestingly, the films show preferential perpendicular ordering of the easy magnetic axis (Figure 40).

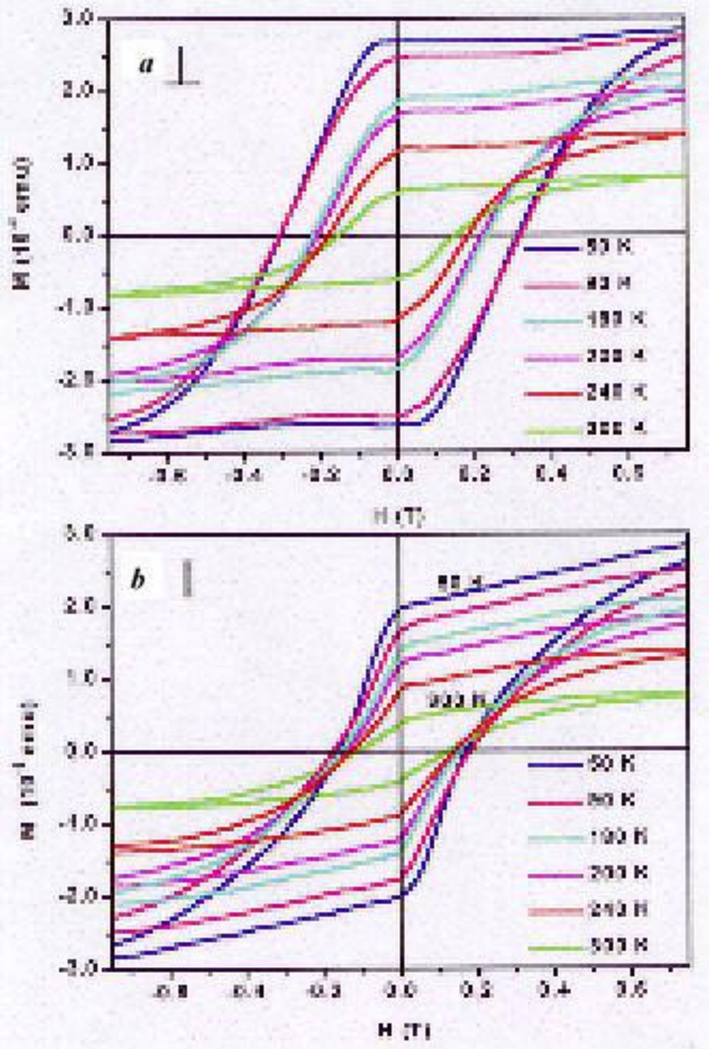


Figure 40. Hysteresis loops from a citrate-capped *g*-Fe2O3 film at various temperatures with the substrate held (***a***) perpendicular and (***b***) parallel to the applied field direction. Note that the hysteresis loops are steeper and wider in the perpendicular orientation.

Thus, the coercivity is larger in the perpendicular orientation. Small perpendicular magnetization exhibited by the nanocrystal films is of great value in magnetic recording and other applications13. We have found that the nanocrystals of metals such as gold dispersed in water can be used for nanolithography by the dip-pen process14. In this technique, Au nanocrystals deposited on the AFM cantilever dissolve in the water meniscus between the tip and the substrate (Figure 41).

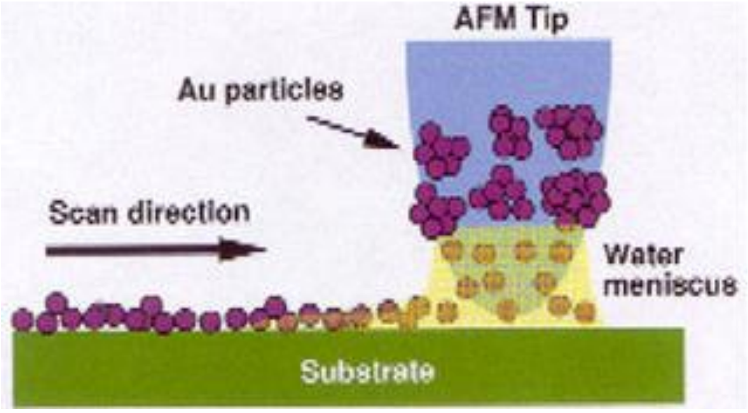


Figure 41. Schematic illustration of the dip-pen process. Au nanocrystals deposited on the cantilever dissolve in the water meniscus between the tip and the substrate.

The dissolved nanocrystals are transferred to the substrate, when the tip is slowly scanned across the surface. Aggregates of nanocrystals are formed on the substrate upon evaporation of the water layer. The dissolved nanocrystals are transferred to the substrate when the tip is slowly scanned over the surface. Aggregates of the nanocrystals are formed on the substrate upon evaporation of the water layer. In Figure 42, we show the AFM image of a line

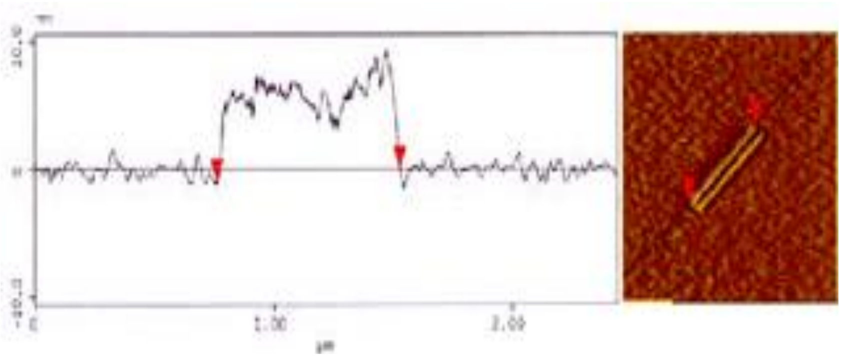


Figure 42. A plot of the cross-sectional profile along a line made of Au nanocrystals shown in the AFM image. The area plotted is indicated in the AFM image alongside.

(35 nm × 750 nm) drawn in this manner along with a plot of the crosssectional profile. The small width of the line obtained by this method is gratifying. The liquid–liquid interface promises to be a universal medium for the synthesis of nanocrystals and thin films of a variety of materials. The results obtained so far fully support such an expectation. The various subtle reaction parameters permit the required control over the size distribution and properties of the nanocrystals obtained by thismethod. Two potential applications of nanocrystals have been demonstrated, one dealing with perpendicular magnetization of *g*-Fe2O3 films and the other with nanolithography using Au nanocrystals.

V. A new Approach to the Synthesis of Nanocrystal Conjugated Polymer Composites

V. A NEW APPROACH TO THE SYNTHESIS
OF NANOCRYSTAL CONJUGATED
POLYMER COMPOSITES

A novel one pot process has been developed for the preparation of PbS nanocrystals in the conjugated polymer poly 2-methoxy,5-(2 - ethyl-hexyloxy-p-phenylenevinylene) (MEH-PPV). Current techniques for making such composite materials rely upon synthesizing the nanocrystals and conducting polymer separately, and subsequently mixing them. This multi-step technique has two serious drawbacks: templating surfactant must be removed before mixing, and co-solvent incompatibility causes aggregation. In our method, we eliminate the need for an initial surfactant by using the conducting polymer to terminate and template nanocrystal growth. Additionally, the final product is soluble in a single solvent. We present materials analysis which shows PbS nanocrystals can be grown directly in a conducting polymer, the resulting composite is highly ordered and nanocrystal size can be controlled.

Introduction

Several groups have blended nanocrystals with conjugated polymers for use in optoelectronic devices [1, 2]. Recently, we developed a new **synthesis for lead sulfide (PbS) nanocrystals in the conjugated polymer poly 2-methoxy,5- (2 -ethyl-hexyloxy-p-phenylenevinylene) (MEH-PPV)** [3]. The current techniques for making nanocrystal: conjugated polymer composite materials rely upon synthesizing nanocrystals separately, and then mixing them with the conjugated polymer [4].

This approach has two shortcomings: firstly, a surfactant must be used to control nanocrystal size and shape. Some of the surfactant becomes incorporated into the final nanocrystal and conjugated polymer mix, which inhibits efficient charge transfer. Secondly, the mixing approach requires the use of co-solvents, which can adversely affect nanocrystal solubility and polymer chain orientation. The major advantage of the new method we describe in this paper is that it eliminates the need for an initial surfactant to terminate nanocrystal growth, and also eliminates the need for subsequent transfer to the conjugated polymer. A similar method has been proposed by Milliron et al. [5] which utilizes an electro-active surfactant. Although our method does not allow tight control of nanocrystal size distribution, it does allow more intimate contact between nanocrystal and the conjugated polymer backbone, which we believe will enhance electronic coupling between the two components and hence improve charge transfer in the system. It is also a significantly less complicated synthetic route. Our novel approach uses the conjugated polymer MEHPPV to control the nanocrystal growth and passivate surface states. MEH-PPV has a high hole mobility and low electron mobility [6]. This relative imbalance limits the performance of any optoelectronic device based upon the material. Nanocrystals, by acting as a percolated high mobility pathway for electrons, offsets this imbalance [7]. It is thought that photoexcited charge separation occurs at the nanocrystal-polymer interface [8]. Hence, the conjugated polymer acts as a colloidal template, and also as the continuous conductive matrix through which photogenerated charges are transferred to the external circuit.

We choose lead sulphide (PbS) as the inorganic material because, in the quantum regime, it has a broad band absorption [9]. Additionally, the electrons and holes are equally confined in PbS nanocrystals, [9] and they been shown to exhibit long excited state lifetime [10]. In this paper we discuss new results from our most refined synthesis to date. In particular we show how polymer molecular weight and solvent ratios can be used to control nanocrystal size.

Experimental

The nanocrystal: conjugated polymer composite was prepared as follows: A sulphur precursor solution was prepared by dissolving 0.08g of sulphur flakes in 10ml of toluene. The mixture was stirred and degassed with argon for 1 hour. In a typical synthesis, 9ml of toluene, 0.01g of 80,000 Daltons average molecular weight MEH-PPV, 3ml of di-methylsulfoxide DMSO and 0.1g of lead acetate were mixed and degassed with argon at 100 ºC for 2 hours in a 25 ml three-neck flask connected to a Liebig condenser. All materials where purchased from Sigma Aldrich and used without further purification. The resultant solution was bright orange in colour with no precipitate or solvent separation. With the solution at 160 ºC, 1ml of the sulphur precursor was injected. The reaction took approximately 15 minutes to reach completion upon which a brown solution resulted. The product was cleaned to remove excess lead or sulphur ions, DMSO and low molecular weight MEH-PPV by adding the minimum amount of anhydrous methanol to cause precipitation of the composite material. The sample was centrifuged and the supernatant removed. The precipitate was then redissolved in the desired solvent (for example toluene or chlorobenzene). Through the reaction 0.2ml samples where taken every three minutes and the reaction halted by injecting into toluene at ambient temperature. This synthesis is referred to as 3:1, Toluene: DMSO henceforth. The synthesis was repeated twice with a single variation each time. The first used 22,000 Daltons MEH-PPV instead of 80,000 Daltons and the second used 8ml of toluene and 4ml of di-methylsulfoxide DMSO (refered to as 2:1, Toluene: DMSO). Transmission electron microscopy (TEM) was carried out using a Tecnai 20 Microscope. Samples where prepared by taking the cleaned product, diluting it and placing a drop on an ultra thin carbon coated copper grid (Ted Pella) with the Formvar removed. A Perkin-Elmer λ40 UV-Visible Spectrophotometer was used to obtain absorption spectra of spun-cast films.

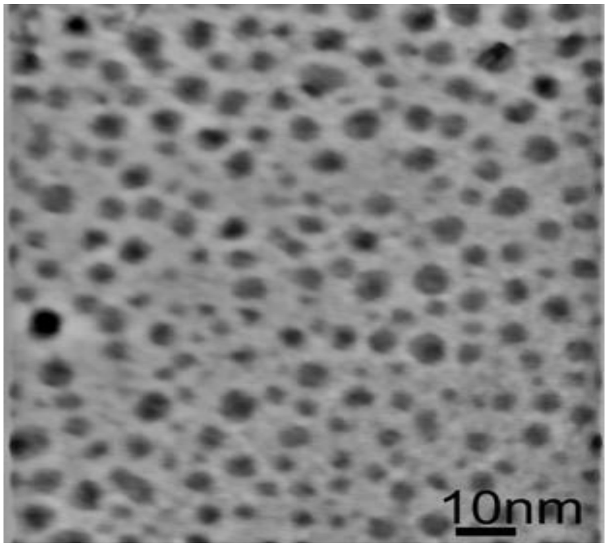


Fig. 43. TEM image of a field of nanocrystals prepared with 3:1, Toluene: DMSO and 80, 000 Daltons MEH-PPV.

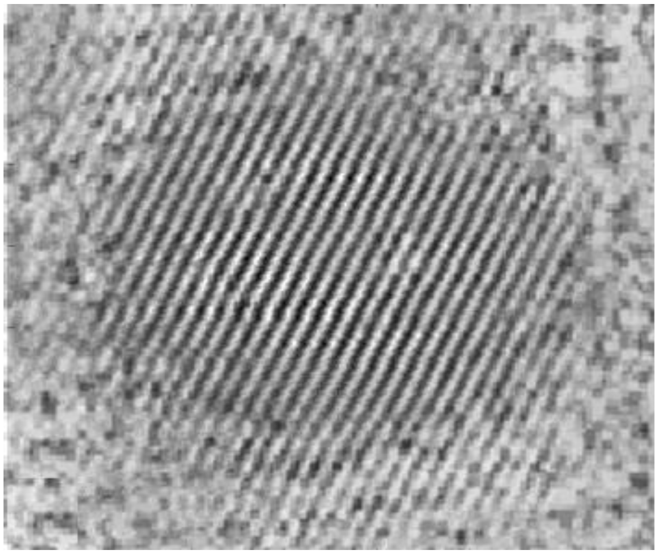


Fig.44. High resolution TEM image of the lattice planes in a single nanocrystal prepared with 3:1, Toluene: DMSO and 80, 000 Daltons MEH-PPV.

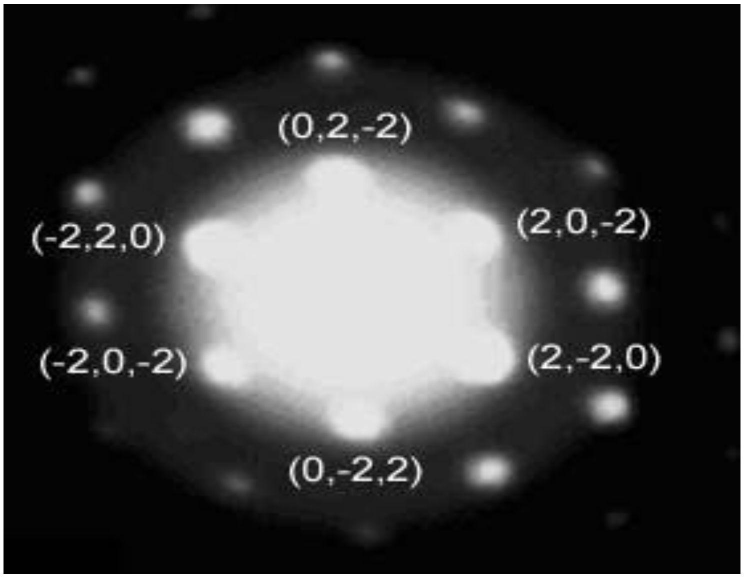


Fig. 45. Selected area diffraction image using a 2µm aperature on a field of nanocrystals prepared with 3:1, Toluene: DMSO and 80, 000 Daltons MEH-PPV. MEH-PPV has an absorption edge at around 560nm.

Results and Discussion

TEM was used to gain an understanding of the nanocrystal growth and quality. Figure 43 shows that nanocrystals are formed and they are non-aggregated with an average size of 4nm (±2nm).

Figure 44 shows the crystal lattice of an individual nanocrystal and demonstrates a high degree of crystallinity. Figure 45 shows a 2µm selected area diffraction pattern of a field of nanocrystals.

The diffraction corresponds to the lattice parameter and pattern of cubic PbS looking down the [1,1,1] zone axis. Usually samples prepared from colloidal solutions display only circular poly-crystalline electron diffraction patterns. The diffraction pattern in figure 3 would tend to indicate a low degree of orientational anisotropy at the ensemble level. These are similar results to those reported by Berman et al. [11] who showed that an ordered array of nanocrystals could form in a polymer matrix. Figure 46 shows how the absorption changes as PbS nanocrystals assemble through the reaction.

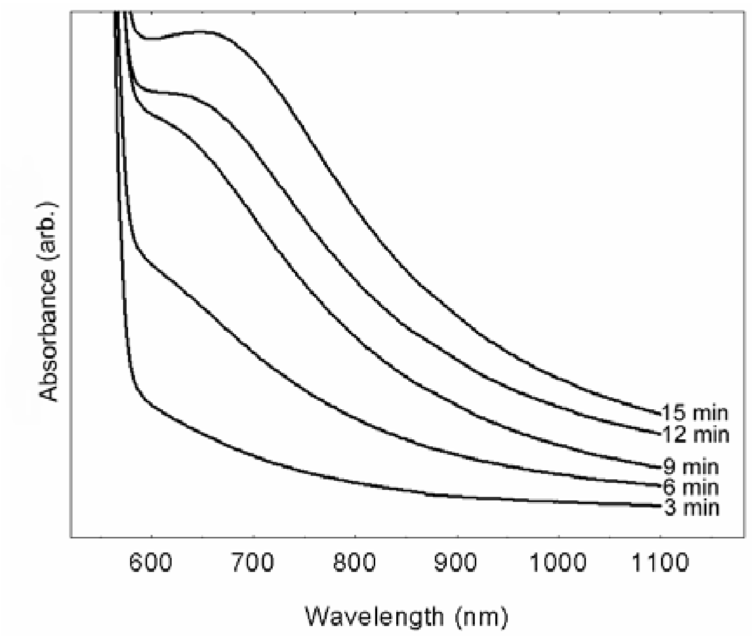


Fig. 46. Change in absorption as reaction proceeds, prepared with 3:1, Toluene: DMSO and 80, 000 Daltons MEH-PPV.

This results in an extension of the absorption into the near IR. The absorption edge corresponds to theoretical predictions for PbS nanocrystals of between 4 and 6 nm. With respect to kinetics, we find that nanocrystal growth is dependent on reaction temperature, reaction time, polymer chain length and polymer solvation. In a standard nanocrystal synthesis, growth control is derived from a combination of electrostatic effects from the surfactant functional groups (eg phosphine), and the steric effects of the long surfactant chain (typically C18 to C24). MEHPPV has no charged functional groups which could electrostatically control nanocrystal growth. Therefore we believe that growth is predominantly influenced by steric effects of the long chain MEH-PPV. Not surprisingly, the rate of reaction is greater at elevated temperatures due to increased solubility and reactivity of the precursors. Figure 47 shows that using 22,000 Daltons MEH-PPV produces larger nanocrystals. The MEH-PPV used in all our reactions is unpurified and contains a spread of molecular weights; this we believe influences the size dispersity of nanocrystals.

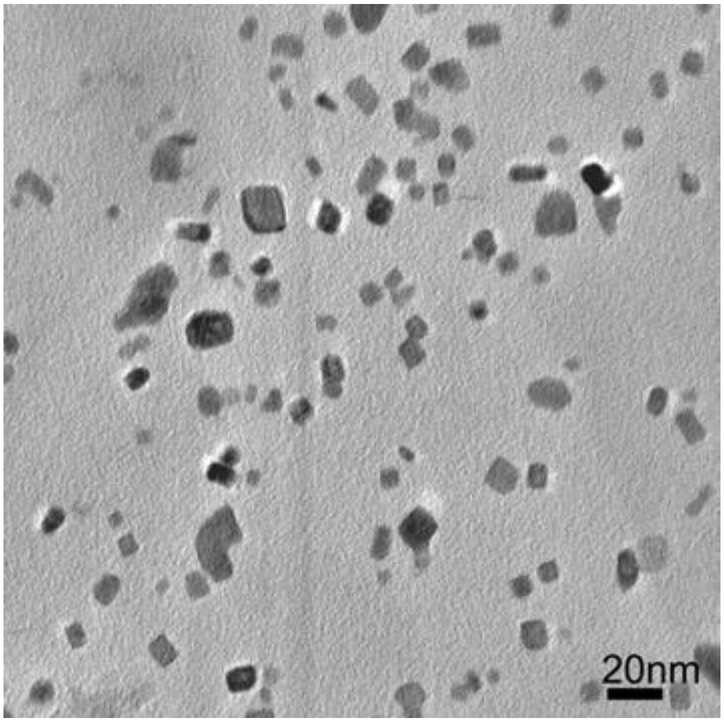


Fig. 47. TEM image of a field of nanocrystals, prepared with 3:1, Toluene: DMSO and 22, 000 Dalton MEH-PPV. If the ratio of Toluene to DMSO used in the reaction is changed from 3:1 to 2:1 we find that the reaction kinetics change as shown by the time evolution absorption graph in figure 48.

Note the red shift of the nanocrystal absorption edge, we attribute this to a change in mean nanocrystal size . Further microscopy studies are underway to determine the size of nanocrystals at each stage of the reaction.

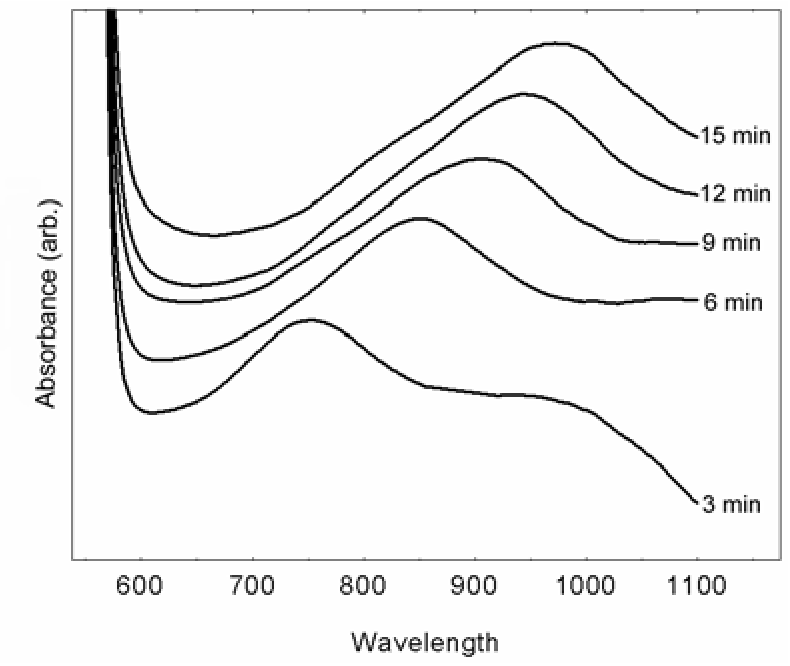


Fig. 48. Change in absorption as reaction proceeds, prepared with 2:1, Toluene: DMSO and 80, 000 Daltons MEH-PPV.

Conclusions

In conclusion we have demonstrated that it is possible to make nanocrystals in a conjugated polymer by a simple single step process without the need for additional surfactants. The nanocrystals self assemble, are highly crystalline and have absorption characteristics as predicted by theory. Initial results tend to indicate that we can tune the nanocrystal size by a combination of solvent ratios and time.

Although this method seems particularly suited to PbS in MEH-PPV, it could potentially be applied to other sorts of nanocrystals e.g. CdSe and other conjugated polymers. Further work is underway to understand the complex dynamics of nanocrystal growth using different polymer molecular weights, purifying the polymer to yield a narrower distribution of molecular weights, and using other solvent systems in a bid to control nanocrystal size and dispersity. We envisage device applications in photovoltaics in particular. It is worthy of note that we have recently demonstrated a solar cell with ~1% power conversion efficiency. These results are to be presented elsewhere.

Acknowledgments

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The objective of the authors :

is to use semiconductor nanocrystals (also known as quantum dots) instead of (or in addition to) dye molecules to produce color in fibers and perhaps to use them as optical brightening agents as well. In semiconductor nanocrystals, the onset of absorbance and emission maximum shift to higher energy with decreasing size of the particles. Such a shift begins to occur in many quantum dots when the size gets to be less than 10nm. Thus it is possible to create different size particles made from a single material with different optical properties that cover the entire visible region of the electromagnetic spectrum. It is this property that we propose to use to our advangate as colorants for fibers. These nanocrystals are quite stable with high quantum yeild, a narrow emission and last longer in comparison to conventional fluorescent dye molecules. Hence, semiconductor nanocrystals might prove to be quite useful as substitutes for dyes and optical brightners that are commonly used to create and enhance the appearance of fabrics. In addition, we will use collodial crystals, impregnated with quantum dots to provide color to the fibers and also to use them as sensors for a variety of applications that does not require high strength.

Introduction:

Color has usually been imparted to fabrics by dyeing the fibers with suitable dye molecules. Such a process of providing color is usually denoted as subtractive mixing. There are a variety of objects in nature that are colored largely because of the physical structure of the substrate, where the dimensions of the structures that are responsible for providing color is on the order of the wavelength of visible light [Srinivasarao, *Chemical Reviews,* **99,** 1935-1961 (1999)]. Many colorful biological substrates, like butterfly wings and beetle exocuticles, interact with light to produce the color that is seen [Srinivasarao, *Chemical Reviews,* **99,** 1935-1961(1999)]. In contrast to color produced by subtractive mixing, those produced by interference or diffraction are quite angle dependent and pure when plotted on a CIE chromaticity diagram.

The main theme of this work is to use semiconductor nanocrystals, and nanocrystal impregnated colloidal crystals as colorants and stable optical brightners. One can imagine two different ways of attaining coloration of fibers by quantum dots: (a) functionalized quantum dots can be diffused into the fiber from aqueous media or (b) they can be mixed with the polymer pellets and spun into fibers that will contain the quantum dots. One can also produce color by having dyes mixed with the quantum dots to produce a spectacular array of color effects that cannot be obtained using dyes or pigments alone. We intend to pursue all the above mentioned paths for generating the desired color. To our knowledge no work has been done using semiconductor nanocrystals as colorants in fibers. Recently however, QD-Polymer composites have been made [1].

The physics and optics of semiconductor nanocrystals have been studied quite extensively [2-5]. Among the many properties that change, the most remarkable is the dramatic change in the optical properties as a funtion of size. As the size decreases the electronic excitations shift to higher energies (lower wavelengths) due to quantum confinement effects, leading the observed changes in the optical properties. The size of nanocrystals begins to have an effect on the physical properties around 10nm. For nanocrystals below 10nm in size, it is well known that the emission becomes a function of their size. The emission is usually quite narrow in comparison to dye molecules. These nanocrystals have the same crystalline structure as that of the extended solid that one is familiar with. The emission can be controlled with the use of different morphologies for the nanocrystal, for example by having a core that is made from one semiconductor with a shell of another semiconductor material.

Particles with CdSe core with ZnS shells with a mercaptoacetic acid funcitionality have been made and used to covalently couple to proteins [6]. Such studies have shown that one can control the emission characteristics of these nanocrystals by choosing the appropriate semiconductor material, so that one can have emission across the entire visible range [6]. Such particles have recently been used to study biological samples. In this case it was necessary to make the particles water soluble so that the particles could diffuse in aqueous media. The following are some of the advantages offered by semiconductor nanocrystals or quantum dots:

- Size control of emisson

- Morphology control of emission (Core-shell particles)

- Easily modified surface chemistry (Solubility)

- Amenable to be used in conjuction with a conventional dye molecule (Additive + Subtractive mixing).

Results:

Our initial studies of polymer dyeing with quantum dots have involved

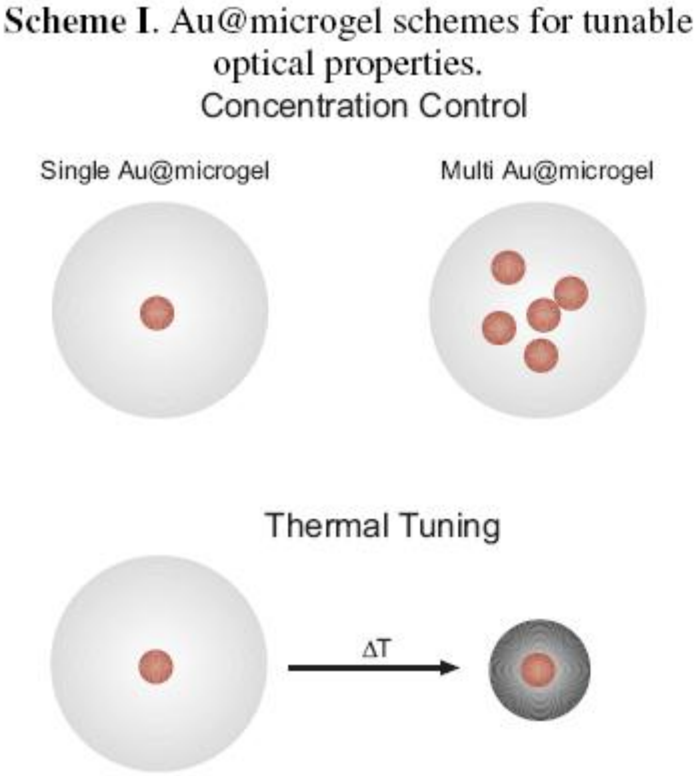

Fig.49. Au@microgel schemes for tunable optical properties.

National Textile Center Annual Report: November 2001 C00-G03 3 C00-G03 4 brightly colored (but non-emissive) metal nanoparticles coated with low refractive index hydrogel layers. While such materials bear little relation to polymers used in the textile industry, they have many advantageous properties in terms of ease of synthesis, tunability, and optical characterization. The specific system studied is that of 12-nm diameter Au particles coated with a thick (~80 nm) layer of poly-N-isopropylacrylamide (p-NIPAm) to yield a monodisperse (<15% polydispersity) sol of polymer-clad Au particles. In aqueous media, p-NIPAm displays a temperature-dependent degree of solvation which can be used to thermally tune the refractive index of the cladding (Scheme I). In this fashion, we can elucidate the optical properties of many different dielectric/metal composites from a single colloidal sol. Furthermore, we can easily control the number of Au particles per dielectric sphere, thereby allowing easy interrogation of “particle dye” concentration effects. Figure 1 shows representative UV-Visible extinction spectra for bare Au particles, and polymer particles with two different Au concentrations (25-fold difference). It should be stated that all Au particles are associated with a polymer sphere; no free Au exists following polymerization. A number of key features in these spectra should be noted. First, the bare Au particles display the typical plasmon absorption band at about 520 nm; a solution of these particles is a deep burgundy color. The dielectric-coated particles, however, have a broad scattering background that largely obscures the Au plasmon absorption. Indeed, at the low Au concentration, the band is completely invisible. These spectra do not accurately reflect the visual appearance of the

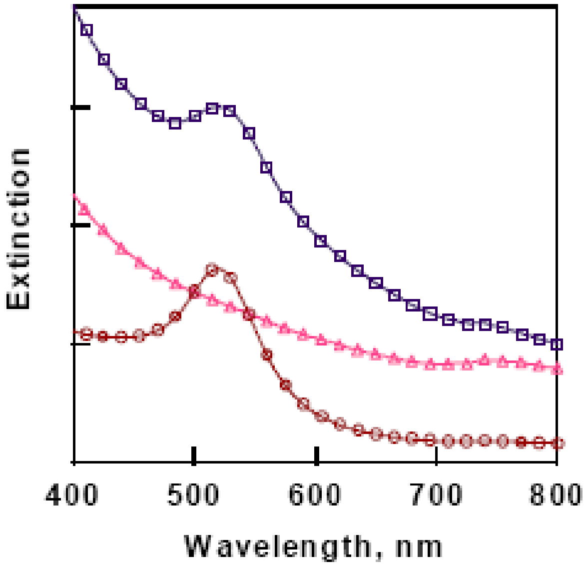

Figure50 . Extinction spectra for colloidal sols of bare Au (circles), low Au concentration polymer particles (triangles, approximately one Au particle per sphere), and a sample with 25-fold higher Au concentration (squares).

samples, however. The low Au concentration sample is a pinkish material, while the higher concentration yields an almost purple polymer solution. The combination of light transmission, reflection, and diffuse scattering yield samples that have very different visual qualities. We are currently investigating the effect of cladding refractive index and Au particle size on the optical properties of these materials. In the past year we have been investigating the use of periodic dielectric structures, specifically colloidal crystals, for use in diffractive (non-chromophore based) textile colorant applications. Colloidal crystals or artificial opals are now widely used in the fabrication of

The building blocks for these soft colloidal crystals are microgels composed of the thermoresponsive polymer poly-N-isopropylacrylamide (pNIPAm) crosslinked with N,N’-methylenebisacrylamide. Monodisperse, spherical particles were prepared by precipitation polymerization in aqueous media as described previously. Using this method, the resultant particle size can be continuously varied from ~50-nm to 1-μm diameter by controlling the surfactant and initiator concentrations. For typical crosslinking densities of 2 mol-%, the resultant microgels undergo an ~15-fold decrease in volume due to water expulsion at the volume phase transition temperature (32 °C). photonic materials for a variety of applications, largely because of the relative ease with which such structures can be assembled. Furthermore, the ability to tune the color of reflected light is easily accomplished by either changing the particle size, spacing, or in the case of the hydrogel colloidal crystals developed in the Lyon group, by changing the compression of deformable particles.

The assembly of close-packed colloidal crystals takes place via a simple multistep process in which the thermoresponsivity of the component nanoparticles is exploited to obtain ordering. Initially, a solution of hydrogel nanoparticles is concentrated via centrifugation at a temperature below the phase transition temperature (25 °C). This produces a polymer mass at the bottom of the tube that is optically transparent with a faint blue, green or red opalescence, where the

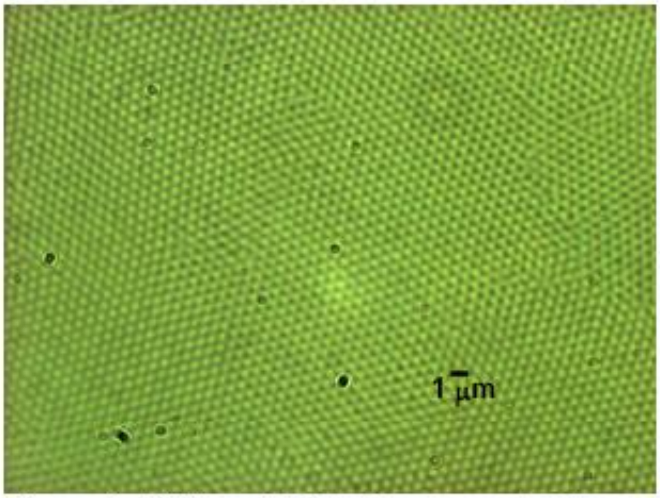

Figure 2. Differential interference contrast image of a hydrogel photonic crystal prepared from ~700-nm diameter pNIPAm microgels.

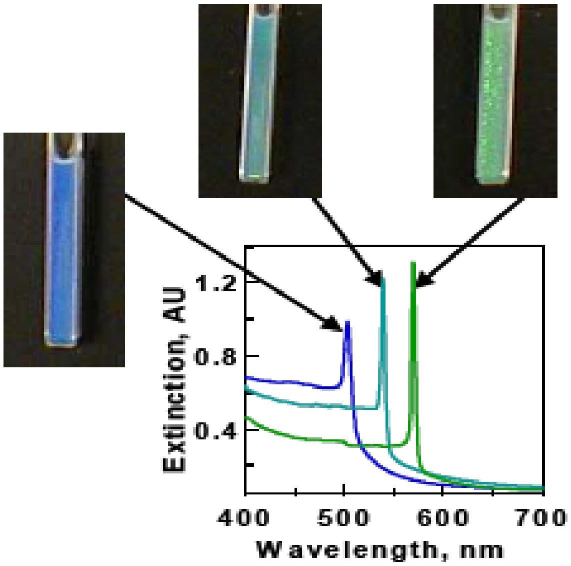

Figure 3. Extinction spectra and corresponding photographs of wavelength-tuned hydrogel photonic crystals.

specific color properties depend on the initial particle concentration, centrifugation time, particle size, and centrifugation speed.The volume phase transition can then be used to anneal defects out of the crystal or to make a processable photonic material. Above the volume phase transition, the material is a low viscosity fluid, as the particles occupy a low volume fraction of the material. However, when lowering the temperature swells the particles, the viscosity increases dramatically, thereby “locking” the material in place. Post treatment such as photo crosslinking can then be used to create a temperature stable and permanent color element.

A typical image (obtained by differential interference contrast microscopy) of a hydrogel colloidal crystal is shown in Figure 51. This image illustrates that the crystal is composed of a highly ordered, close-packed arrangement of spherical hydrogel particles. Since the component particles are soft and hydrated, the lattice spacing can be manipulated by changing the water content of the particles. This effect is illustrated in Figure 52, where a single particle size has been used to create crystals of three distinct colors.

Using this technique, we have demonstrated the ability to tune the color of a crystal over >150 nm. Furthermore, these materials display brilliant opalescence when the angle of observation is changed, thereby providing opportunities for even greater control over the color properties

.

Our work to this point has allowed us to understand in detail the processes of photonic crystal assembly, defect annealing, color tuning, and crystal processing. We are now continuing these studies in the context of fiber coating and fiber filling for colorant applications. For example, hollow core fibers will be filled by capillary action when the crystals are in their fluid form, followed by cooling to the viscous form. We will then study the color properties of these fibers as a function of internal core diameter, original crystal color, fiber conformation (to study angle dependent opalescence), and fiber refractive index. In parallel, we will investigate the coating of solid fibers with both standard and complex shapes, to investigate the color dispersion properties in the presence of diffractive, wavelength selecting coatings.

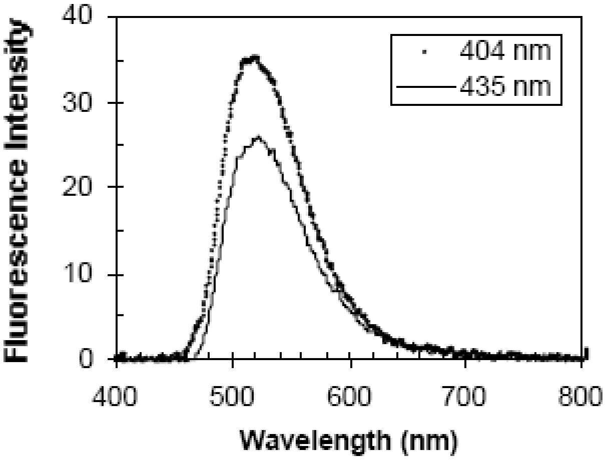

Figure 54. Extinction spectra and corresponding photographs of wavelength-tuned hydrogel photonic crystals. C00-G03 6 6 National

Textile Cent C00-G03 7 study the optical properties of such fibers.

Together, these studies will allow for a better understanding of how diffractive colorants can be used to impart non-chromophoric optical properties to textile fibers. We have also obtained fibers which have photoluminescent particles and have begun to The fibers and the photoluminescent particles were obtained from Score Technologies. A typical emission spectra is shown in Figure 4 obtained using a microspectrometer. The fiber emits in the green-yellow part of the visible spectrum. We are interested in developing an understanding of the optical properties of the pigments, the pigments in the fiber and effect on environment.

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Use of Quantum Dots to Produce Colour in Fibres

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