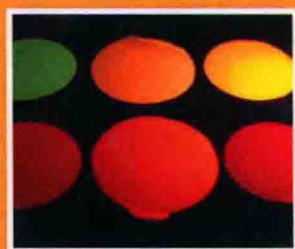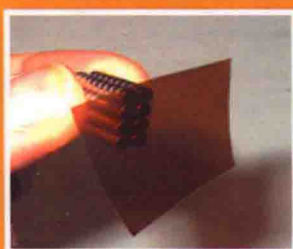# Nanocomposites

In Situ *Synthesis of Polymer-Embedded Nanostructures*

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PREFACE

New physical and chemical properties arise in solid matter when it is reduced to a nanoscopic scale. Most of these novel characteristics (e.g., electron confinement, size-dependent magnetism, enhanced electric field near the surface, surface plasmon resonance) can be exploited for advanced functional applications in many technological fields. All material types (ceramic, polymers, metals, etc.) acquire unique properties at a nanometric scale; however, the most dramatic change in properties as a consequence of size reduction is evidenced by metals and semiconductors. Consequently, research activity in nanostructured materials worldwide focuses mainly on metallic and semiconductive nanoparticles. Because of their very small size, metal and semiconductor nanostructures are difficult to handle, store, and use. Single nanostructures can be manipulated by special techniques like surface tunneling microscopy (STM), dielectrophoresis, and magnetophoresis. However, even the fabrication of quite simple macroscopic devices (e.g. single-electron transistors) by these approaches results really difficult. The spontaneous arrangement of perfectly identical nanostructures in regular arrays (self-organization) is an important tool for the realization of devices based on nanosized objects. However, only a few spherically shaped nanosized solids are able to self-organize in two- or three-dimensional macroscopic structures. Nanostructures can be readily used if they are supported on special ceramic substrates or embedded inside organic or inorganic matrices (the embedding phase can also be a liquid, as in the case of ferrofluids). Supported nanostructures are used mainly in the fabrication of heterogeneous catalysts and special gas-absorbing media, but in all other cases the preferred approach to handle nanoparticles is to have them embedded.

In addition polymer-embedded nanostructures are chemically protected and stabilized. Practically, all atoms and molecules in nanosized solids are located at the surface. Thus, they are coordinatively unsaturated and therefore extremely reactive. For example, oxidation and contamination by absorption of small molecules present in air (e.g., SO_2) is a very fast process for metallic nanopowders. In addition, reactions involving nanosized solids stoichiometrically behave and also noble metals like gold, palladium, and platinum are not anymore chemically inert on a nanometric scale. Embedding of nanoparticles is a very simple way to solve all reactivity problems.

Toxicity is another important aspect concerning nanostructures, and the embedding process also presents a valid solution to this problem. This is an emerging topic in the field of nanotechnology and will determine future developments in this research area. Because of toxicity, the handling of large amounts of nanostructures will be very critical and their use in an embedded form represents a really promising approach. The risk of using toxic nanostructures is expressed as the product of hazard and exposure ($R = H \times E$).

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The embedding process reduces exposure, thus decreasing the risk drastically. In the future, embedding of nanostructures will probably be the only safe method for using nanoscopic materials.

So far, research activity on embedded metal and ceramic nanostructures has mostly been done by inorganic hosts (typically glasses). Inorganic glasses adequately protect nanoparticles, but they have two main disadvantages: (i) processing of these nanostructured materials is quite complex for the high temperatures involved, and (ii) glasses have scarcely tunable physical and mechanical characteristics. Polymer embedding of nanostructures shows several advantages in comparison with glass embedding. As polymer embedding requires only moderate temperatures for processing and has wide-ranging physical characteristics, they allow the nanocomposites to be suitable for many technological applications. For example, polymers can be dielectric media or dielectric conductors, hydrophobic or hydrophilic solids, hard–fragile (thermosetting resins), soft-plastic (thermoplastics), or elastic (rubbers) materials. Such a variety of properties is of fundamental importance to design functional materials. In addition, polymers are permeable to small molecules, which presents great potential in the fabrication of chemical sensors for gasses and liquids.

Unlike their chemical properties, a number of physical properties of nanostructures remain unmodified after polymer embedding (e.g., magnetic, optical, dielectric). In addition, owing to the large interface area, there are several polymer characteristics that are affected by filling with nanosized solids (e.g., glass transition temperature, crystallinity content, flame resistance, and gas permeability).

Nanostructures have tremendous potential for functional applications. However, the use of these materials is still very limited due to the difficulty in tuning their properties by controlling their morphological/structural features. In addition, since the collective properties of nanosized systems strongly differ from those of single particles, the special topology realized in the nanocomposite material represents a further way of modulating functional characteristics. Such a unique composite class represents a revolutionary approach in the science and technology of materials, and it has enormous potential for advanced functional applications. In fact, polymer-embedded nanoscopic structures like metal clusters, semiconductors, quantum dots, fullerenes, fine granular superconductors, ceramics, nanoparticles, nanotubes, nanoshells, graphenes, etc. can be exploited for functional applications in a variety of technological fields (e.g., optics, electronics, and photonics). However, all aspects concerning functionality control, multifunctionality, etc. are known only at a pioneering level, and systematic investigations are required.

The functional properties of polymer-based nanocomposites arise from the nanoscopic filler or from a combination of polymer and filler characteristics. Different approaches are available for the preparation of nanostructures; however, chemical methods are most effective for the large-scale production of these special solid structures. In fact, chemical methods allow bulk quantities of reproducible material to be obtained. Since functionality control is extremely important and the properties of solid phases at a nanoscopic scale are strictly dependent on size and shape, it is imperative to develop preparative schemes that allow one to have control over the product morphology.

Nanocomposites are potentially useful for many advanced functional applications in different technological fields because of (i) the optical transparency related to the small filler size, (ii) the unique nanophase functionality due to surface and confinement effects, and (iii) the variety of properties that organic–inorganic hybrids may have. A description for the main application areas follows.

Owing to large surface development, metal clusters have a special property known as surface plasmon absorption. Electron plasma oscillates at metal surface under the action of electric field of light, and resonances are possible at particular frequencies. Consequently, metal nanoparticles can absorb light by this special mechanism. Clusters of coin metals (gold, silver, copper) and some of their alloys (e.g., Pd/Ag and Au/Ag) strongly absorb light; therefore, they can be used as pigments to fabricate optical limiters (color filters, UV absorbers, etc.). The main advantages in comparison with traditional organic dyes are as follows: (i) they have very intensive coloration (e.g., the optical extinction of silver is c. 3×10^{11} $M^{-1}cm^{-1}$), (ii) high transparency, and (iii) light fastness and (iv) provide the possibility of making ultrathin colored films. The use of alloyed metal clusters (e.g., gold–silver and platinum–silver alloys) makes it possible to fine-tune the maximum absorption frequency, covering the full UV-visible spectral range.

When particles are uniaxially oriented inside the matrix, two different resonance frequencies are possible (longitudinal and transversal plasma oscillations). Such property can be exploited for optical polarizer fabrication. Frequently, the uniaxial orientation of filler is achieved simply by cold-drawing of raw nanocomposite material (e.g., polyethylene-based materials). This regular morphology produces polarization-dependent optical properties, which allows one to make optical filters that are able to change color by modifying the light polarization direction. A number of electro-optical devices are obtained by combining liquid crystal displays with these special color filters (e.g., multicolor single-pixel displays).

Optical sensors are very promising devices since their use does not require an electronic apparatus. Different types of optical sensors (e.g., chemosensors, pressure sensors, and thermochromic materials) can be based on polymer-embedded gold or silver clusters. In these nanocomposite materials, the surface plasmon resonance frequency of metal clusters is strictly related both to interparticle distance and the host medium refractive index (r.i.). Polymers may undergo significant structural changes because of external stimuli (e.g., pressure increase, temperature changes, and fluid absorption). These structural modifications may influence the surface plasmon resonance of guest metal, producing a visible color variation. Thermochromic materials are systems made of metal clusters topologically organized in an amorphous polymer in the form of extended planar aggregates. Metal clusters are not sintered together but are separated by a thin organic coating layer. Below the organic coating melting point, the material is characterized by a "collective" surface plasmon absorption of aggregated clusters, while above this temperature the expansion of the coating does not allow particles to interact with each other, leading to the coloration of "isolated" particle. Polymers may swell by absorption of fluids having comparable polarity. If these polymers incorporate Au or Ag clusters, their coloration changes during swelling owing to interparticle distance and r.i. modification. A variety of plasmon-based chemosensors can be made using polymers of

different polarities. These materials are especially useful for clinical applications as disposable rapid test strips. Rubbers are amorphous polymers that crystallize under stress, and when filled by a great amount of coin metal clusters, change coloration depending on the stress applied. Such systems can be used as pressure sensors and devices to measure deformation. In general, polymer sensors are convenient due to their low price, disposability, easy fabrication, possibility to be applied by spry, etc.

Thermal reflectors are important devices that protect electronic equipment against exposure to intense solar light or fires, cryotechnological applications, solar energy exploitation, military uses (IR shields), etc. The possibility of fabricating these systems using polymers is of fundamental importance since polymers can be manufactured as textiles, applied as varnish, easily processed in a variety of shapes, and used as adhesives, sealants, etc. Gold-based nanocomposites with special topological features (i.e., presence of extended planar aggregates) show a strong ability to reflect near infrared (NIR) radiation. These materials can be easily produced on a large scale by thermal decomposition of special gold precursors. If optical plastics are used, the resulting nanocomposite material will serve as an effective infrared barrier (heat mirrors) but will be transparent to visible and UV light.

Metal clusters are so small that their nanocomposites are optical media. Nanosized metals are characterized by an r.i. value that ranges from less than 1 to ca. 6 in the visible spectral region. Metals like silver and gold have very low r.i. values ($n_{Ag}=0.01$, $n_{Au}=0.5$), and metals like tungsten and osmium have very high r.i. values ($n_{W}=4$, $n_{Os}=6$). At low filling factors (less than 15% by weight), the r.i. of polymer-embedded metal nanoparticles is given by the linear combination of pure bulk-metal and polymer r.i. values, but a significant deviation from this simple mixture rule has been observed at higher metal loadings. Since all optical plastics have r.i. close to 1.5, the possibility of modifying these values by introducing metal fillers is very important. Polymeric materials with ultra-high/infra-low r.i. values are very useful, for example, for waveguide fabrication (optical fibers require a high-r.i. material for core and a low-r.i. material for cladding). Such plastic fibers offer a number of advantages in comparison with traditional inorganic optical fibers: low-price, good mechanical performance, easily continuous production by coextrusion of molten metal/polymer blends, etc.

Ferromagnetic particles of iron, nickel, cobalt, gadolinium, chromium and manganese alloys, lanthanides, etc. reduced to a nanometric size do not produce scattering phenomena; therefore, they can be embedded into optical plastics to give magnetic materials transparent to visible light. Because of transparency, such magnetic plastics may have important magneto-optical applications such as Faraday's rotators. In particular, dielectric materials like polymers produce low-intensity Faraday's effect (i.e., when placed into an intensive magnetic field they rotate plane-polarized light, but the characteristic Verdet's constant value is low). The presence of a ferromagnetic filler inside these polymers significantly increases the Faraday effect, giving adequate nanocomposite materials for magneto-optical applications like optical windows (ultrafast shutters), optical modulators, optical isolators, etc.

Materials characterized by optical properties depending on the intensity of incident light are strongly required in different technological fields. For example, organic solar cells (e.g., ftalocianine-based devices) may be damaged by exposition to very intensive

sunlight. The protection of these photovoltaic devices from intensive light exposure requires special optical limiters which absorption coefficient behaves non-linearly with light intensity. Polymer-embedded semiconductors, such as lead sulfides (PbS), are ideal material for such an application. Optical filters based on PbS are almost transparent under scarce illumination conditions and develop strongly absorbing properties in the presence of intensive sunlight. In addition to extinction, many other optical properties have been found to nonlinearly behave in optical plastics filled by little amounts of metals and semiconductors (e.g., r.i.).

Polymer-embedded semiconductor nanoparticles (quantum dots) like sulfides and other chalcogenides may emit monochromatic light in the visible spectral region when exposed to ultraviolet radiation. Since the band gap in these semiconductors is size-dependent, the color of emitted light can be tuned by controlling the dimension of the nanoparticle. These nanocomposite materials can be used as high monochromatic light sources for special photonic applications. By incorporating semiconductor nanocrystals in carrier-transporting polymers, an interesting class of photoconductive nanocomposites can be created. The presence of semiconductor nanocrystals enhances the photo-induced charge generation efficiency and extends the sensitivity range, while the polymer matrix is responsible for charge transport. A wide variety of semiconductors (e.g., CdS, GaAs, HgS, InAs, Ga_2S_3, and In_2S_3) and conductive polymers (e.g., polypyrrole, polyvinylcarbazole, polyaniline, polythiophene, and amine-doped polycarbonate) can be combined together for this application.

In conclusion, the physics and chemistry of nanometer-scale objects, and materials and devices that can be obtained from them, represents one of the most important areas of new material research. In particular, the science of mesoscopic metal structures has enjoyed an explosive growth in recent years due to the promise it has shown in major applications in electronics and photonics. Nanostructured metals are characterized by novel properties that are produced by surface and confinement effects. Many of these characteristics can be used to generate polymers with advanced properties. The resulting polymer-based nanocomposites are very promising as advanced functional materials in many technological fields. In addition, they have the processability of polymers, the outstanding electrical and optical properties of metals, and the lack of light scattering of nanometric fillers.

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CONTENTS

1

METAL–POLYMER NANOCOMPOSITES BY SUPERCRITICAL FLUID PROCESSING

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1.1 INTRODUCTION TO POLYMERS, NANOPARTICLES, AND SUPERCRITICAL FLUIDS

Nanoparticles
A nanoparticle is defined by the British Standards Institution as follows:
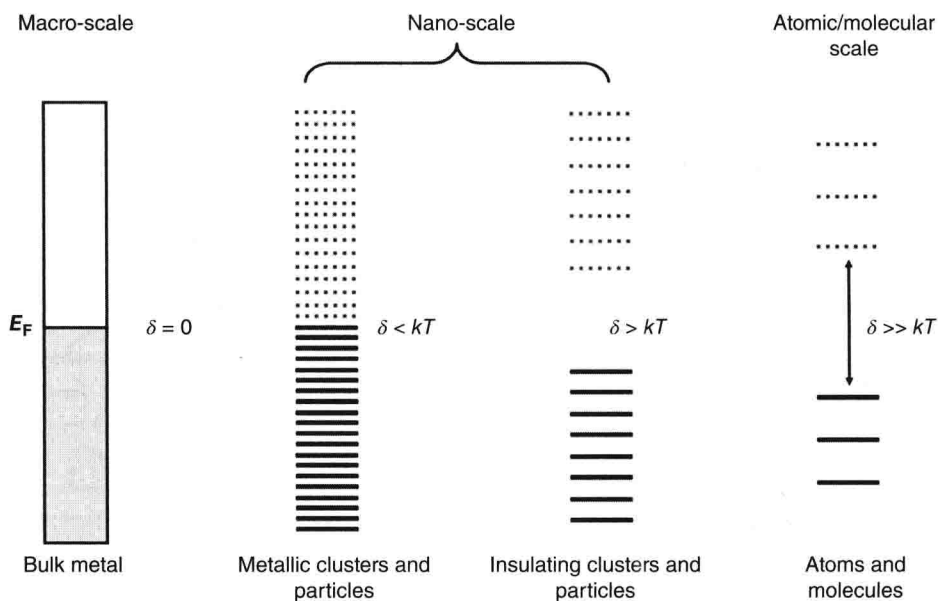*Nanoparticle—particle with one or more dimensions at the nanoscale*
Nanoscale—having one or more dimensions of the order of 100 nm or less
This is in good agreement with how the term is used in general within the scientific community, although there is some degree of ambiguity as to the upper size limit. Particles and materials with the smallest domain sizes up to a micrometer and even several micrometre are sometimes referred to as "nano," although this is becoming less common with the increasing standardization of terminology in nanoscience.

1.2 PROPERTIES

Over the last three decades, nanoparticles have received an increasing amount of research interest. This is due to the unique size-dependent properties of nanoparticles, which are often thought of as a separate and intermediate state of matter lying between

Macro-scale   Nano-scale   Atomic/molecular
                                                                              scale

E_F $\delta = 0$ $\delta < kT$ $\delta > kT$ $\delta \gg kT$

Bulk metal   Metallic clusters and   Insulating clusters and   Atoms and
                      particles   particles   molecules

Figure 1.1. The evolution of the band gap and the density of states as the number of atoms in a system increases (from right to left). E_F is the Fermi energy level of the material and δ is the Kubo gap; see related text. Adapted from Roduner [2]. Reproduced by permission of The Royal Society of Chemistry.

individual atoms and bulk material. The properties of nanoparticles arise as a consequence of the confinement of the electron wave function and of the extremely high proportion of surface atoms—both of these factors are directly dependent on the size of the nanoparticle [1]. Indeed the possibility to control the properties, by tuning the size of the nanoparticle, has been the cause and subject of much investigation. Unlike bulk materials that have constant physical properties regardless of mass, nanoparticles offer unique opportunities for control by varying the diameter and have electronic, magnetic, and optical properties that can be manipulated. These effects occur because the energy levels for small particles are not continuous, as in bulk materials, but discrete, due to confinement of the electron wave function. The physical properties of nanoparticles are therefore determined by the size of the particle, the relatively small physical dimension in which the wave function is confined (Fig. 1.1).

The Fermi energy level (E_F) is the highest occupied energy level of the system in its ground state (lowest energy). The band gap (E_g) of these systems is the energy gap between the highest occupied and lowest unoccupied energy states. In these systems, from discrete atoms to bulk materials, the energy spacings are determined by the extent of the overlap between the electron orbitals of the material. Individual atoms have well-known atomic orbitals. These can combine in molecules to form molecular orbitals and further to form extended band structures, as in metals or semiconductors. The value of E_g is proportional to E_F divided by the number of delocalized electrons in the extended band