

Metal-Polymer Nanocomposites

Edited by

Luigi Nicolais

Gianfranco Carotenuto



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and Biomedical Materials
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CONTENTS

Preface	vii
Contributors	xiii
1 PHYSICAL AND CHEMICAL PROPERTIES OF NANO-SIZED METAL PARTICLES	1
<i>C. N. R. Rao, G. U. Kulkarni, and P. J. Thomas</i>	
2 METAL-CONTAINING POLYMERS: CRYOCHEMICAL SYNTHESIS, STRUCTURE, AND PHYSICOCHEMICAL PROPERTIES	37
<i>L. I. Trakhtenberg and G. N. Gerasimov</i>	
3 CONTROLLED PYROLYSIS OF METAL-CONTAINING PRECURSORS AS A WAY FOR SYNTHESIS OF METALLOPOLYMER NANOCOMPOSITES	75
<i>A. D. Pomogailo, A. S. Rozenberg, and G. I. Dzhardimalieva</i>	
4 NANOSTRUCTURED POLYMERIC NANOREACTORS FOR METAL NANOPARTICLE FORMATION	123
<i>L. M. Bronstein</i>	
5 METAL-POLYMER NANOCOMPOSITE SYNTHESIS: NOVEL <i>EX SITU</i> AND <i>IN SITU</i> APPROACHES	155
<i>G. Carotenuto, L. Nicolais, B. Martorana, and P. Perlo</i>	
6 PLAMON ABSORPTION OF EMBEDDED NANOPARTICLES	183
<i>A. Heilmann</i>	
7 MAGNETOOPTICS OF GRANULAR MATERIALS AND NEW OPTICAL METHODS OF MAGNETIC NANOPARTICLES AND NANOSTRUCTURES IMAGING	201
<i>V. I. Belotelov, P. Perlo, and A. K. Zvezdin</i>	

8	OPTICAL EXTINCTION OF METAL NANOPARTICLES SYNTHESIZED IN POLYMER BY ION IMPLANTATION	241
	<i>A. L. Stepanov</i>	
9	OPTICALLY ANISOTROPIC METAL–POLYMER NANOCOMPOSITES	265
	<i>W. Caseri</i>	
	Index	287

PREFACE

As advanced technologies are expanding, the need for novel functional materials significantly increases. Nowadays, materials with a special combination of properties (e.g., magnetic–transparent, conductive–transparent, catalytic–magnetic, etc.) are strictly required. Materials based on nano-sized metals will surely represent an adequate solution to many present and future technological demands, since they exhibit both novel properties (e.g., plasmon resonance, superparamagnetism, etc.) and unique properties combinations.

Nano-sized metals have special characteristics that can be exploited for a number of advanced functional applications. However, the difficult handling of these incredibly small objects (1–30 nm) has represented a strong limitation to their use. Manipulations of single nanoscopic objects by surface tunneling microscopy (STM), spontaneous self-assembly, and dielectrophoresis are the only available approaches for building functional devices using nano-sized metals. In addition, most of nano-sized metals are very instable: They can aggregate because of the high surface free energy and can be oxidized-contaminated by air, moisture, SO₂, and so on. The embedding of nanoscopic metals into dielectric matrices represents a valid solution to the manipulation and stabilization problems. In the functional field, polymers are particularly interesting as an embedding phase, since they may have a variety of characteristics: They can be an electrical and thermal insulator or conductor, may have a hydrophobic or hydrophilic nature, can be mechanically hard, plastic, or rubbery, and so on. Finally, polymer-embedding is the easiest and most convenient way for nanostructured metals' stabilization, handling, and use. Polymer-embedded nanostructures are frequently termed nanocomposites because of their biphasic nature.

The fundamental knowledge on the preparation and nature of metal–polymer nanocomposites has a long history that is connected to the names of many famous scientists. The oldest technique for the preparation of metal–polymer nanocomposites that can be found in the literature was described in an abstract that appeared in 1835. In an aqueous solution, a gold salt was reduced in the presence of gum arabic, and subsequently a nanocomposite material was obtained in the form of a purple solid simply by coprecipitation with ethanol. Around 1900, widely forgotten reports describe the

preparation of polymer nanocomposites with uniaxially oriented inorganic particles and their remarkable optical properties. Dichroic plants and animal fibrils (e.g., linen, cotton, spruce, or chitin, amongst others) were prepared by impregnation with solutions of silver nitrate, silver acetate, or gold chloride, followed by reduction of the corresponding metal ions under the action of light. Dichroic films were also obtained using gold chloride-treated gelatin that was subsequently drawn, dried, and finally exposed to light. Similar results were obtained when gelatin was mixed with colloidal gold before drying and drawing. In 1904, Zsigmondy (Nobel Laureate in Chemistry, 1925) reported that nanocomposites of colloidal gold and gelatin reversibly changed the color from blue to red upon swelling with water. In order to explain the mechanism of nanocomposite color change, they suggested that the material absorption must also be influenced by the interparticle distance. In addition, around the same time, the colors of gold particles embedded in dielectric matrices was the subject of detailed theoretical analyses by Maxwell Garnett, who explained the color shifts upon variation of particle size and volume fraction in a medium. During the following three decades, dichroic fibers were prepared with many different metals (i.e., Pd, Pt, Cu, Ag, Au, Hg, etc.). The dichroism was found to depend strongly on the employed element, and optical spectra of dichroic nanocomposites, made of stretched poly(vinyl alcohol) films containing gold, silver, or mercury, were presented in 1946. It was assumed already in the early reports that dichroism was originated by the linear arrangement of small particles or by polycrystalline rod-like particles located in the uniaxially oriented spaces present in the fibers. An electron micrograph published in 1951 showed that tellurium needles were present inside a dichroic film made of stretched poly(vinyl alcohol). In 1910, Kolbe proved that dichroic nanocomposite samples based on gold contained the metal indeed in its zero-valence state. Such affirmation was confirmed a few years later by X-ray scattering; in particular it was shown that zero-valence silver and gold were present in the respective nanocomposites made with oriented ramie fibers, and the ring-like interference patterns of the metal crystallites showed that the individual primary crystallites were not oriented. Based on Scherrer's equation, which was developed in this period, the average particle diameter of silver and gold crystallites was determined in fibers of ramie, hemp, bamboo, silk, wool, viscose, and cellulose acetate to be between 5 and 14 nm.

Metals undergo the most considerable property change by size reduction, and their composites with polymers are very interesting for functional applications. The new properties observed in nano-sized metals (mesoscopic metals) are produced by quantum-size effects (i.e., electron confinement and surface effect). These properties are size-dependent and can be simply tuned by changing the dimension. Since the same element may show different sets of properties by size variation, a Three-dimensional Periodic Table of elements has been

proposed. Confinement effects arise in nano-sized metal domains since conduction electrons are allowed to move in a very small space, which is comparable to their De Broglie wavelength; consequently their states are quantized just like in the atoms, and these systems are termed *artificial atoms*. Surface effects are produced because with a decrease in size, matter consists more and more of surface atoms than of inner atoms. As a result, the matter properties slowly switch from that determined by the characteristics of inner atoms to that belonging to surface atoms. In addition, the surface nature of a nano-sized object significantly differs from that of a massive object. Atoms on the surface of a massive crystalline solid are principally located on basal planes, but they transform almost completely in edge and corner atoms with a decrease in size. Because of the very low coordination number, edge and corner atoms are highly chemically reactive, supercatalytically active, highly polarizable, and so on, in comparison with atoms on basal planes.

Because of quantum-size effects, mesoscopic metals show a set of properties completely different from that of their massive counterpart. Particularly interesting is: the size-dependent ferromagnetism and the superparamagnetism characterizing all metals (included diamagnetic metals like silver); the chromatism observed with silver, gold, and copper metals due to plasmon absorption; the photo- and thermoluminescence; and the supercatalytic effect (hyperfine catalysts are characterized by an extraordinarily higher catalytic activity and a different selectivity compared to corresponding fine powders). In addition, because of the band-structure disappearance, metals become thermally and electrically insulators at very small sizes. They are highly chemically reactive (heterogeneous reactions become stoichiometric and new reaction schemes are possible, for example: nano-sized noble metals are very reactive), are super absorbent, and show completely different thermodynamic parameters (for example, they melt at much lower temperatures). Many of these unique chemical–physics characteristics of nano-sized metals leave unmodified after embedding in polymers (e.g., optical, magnetic, dielectric, and thermal transport properties), and therefore they can be used to provide special functionalities to polymers.

A limited number of methods have been developed for the preparation of metal–polymer nanocomposites. Usually, such techniques consist of highly specific approaches, which can be classified as *in situ* and *ex situ* methods. In the *in situ* methods, two steps are needed: First, the monomer is polymerized in solution, with metal ions introduced before or after polymerization. Then metal ions in the polymer matrix are reduced chemically, thermally, or by UV irradiation. In the *ex situ* processes, the metal nanoparticles are chemically synthesized, and their surface is organically passivated. The derivatized nanoparticles are dispersed into a polymer solution or liquid monomer that is then polymerized.

For the comprehension of mechanisms involved in the appearance of novel properties in polymer-embedded metal nanostructures, their characterization represents the fundamental starting point. The microstructural characterization of nanofillers and nanocomposite materials is performed mainly by transmission electron microscopy (TEM), large-angle X-ray diffraction (XRD), and optical spectroscopy (UV–Vis). These three techniques are very effective in determining particle morphology, crystal structure, composition, and particle size.

Of the many techniques that have been used to study the structure of metal–polymer nanocomposites, transmission electron microscopy has undoubtedly been the most useful. This technique is currently used to probe the internal morphology of nanocomposites. High-quality images can be obtained because of the presence in the sample of regions that do not allow high-voltage electron beam passage (i.e., the metallic domains) and a region perfectly transparent to the electron beam (i.e., the polymeric matrix). High-resolution transmission electron microscopy (HRTEM) allows morphological investigations with resolution of 0.1 nm, and thus this technique makes it possible to accurately image nanoparticle sizes, shape, and atomic lattice.

Large-angle X-ray powder diffraction (XRD) has been one of the most versatile techniques utilized for the structural characterization of nanocrystalline metal powders. The modern improvements in electronics, computers, and X-ray sources have allowed XRD to become an indispensable tool for identifying nanocrystalline phases as well as crystal size and crystal strain. The comparison of the crystallite size obtained by the XRD diffractogram using the Scherrer formula with the grain size obtained from the TEM image allows us to establish if the nanoparticles have a mono- or polycrystalline nature.

Most metal clusters are characterized by the surface plasmon resonance, which is an oscillation of the surface plasma electrons induced by the electromagnetic field; consequently, their microstructure can be indirectly investigated by optical spectroscopy (UV–Vis spectroscopy). The characteristics of this absorption (shape, intensity, position, etc.) are strictly related to the nature, structure, topology, and so on, of the cluster system. In fact, the absorption frequency is a fingerprint of the particular metal, the eventual peak splitting reflects aggregation phenomena, the intensity of the peak is related to the particle size, the absorption wavelength is related to the particle shape, the shift of the absorption with increasing of temperature is indicative of a cluster melting, and so on. For bimetallic particles, information about inner structure (inter-metallic or core/shell) and composition can be obtained from the absorption frequency. Differently from *off-line* techniques (e.g., TEM, XRD), this method allows *on-line* and *in situ* cluster sizing and monitoring of morphological evolution of the system. This method has been used also in the study of cluster nucleation and growth mechanisms.

This outline of the principal characterization techniques for nanocomposite materials is far from being complete. Advances in Raman spectroscopy, energy dispersive spectroscopy, infrared spectroscopy, and many other techniques are of considerable importance as well. In fact, the success that nanostructured materials are having in the last few years is strictly related to the advanced characterization techniques that are available today.

Applications of metal–polymer nanocomposites have already been made in different technological fields; however, the use of a much larger number of devices based on these materials can be predicted for the near future.

Because of the plasmon surface absorption band, atomic clusters of metals can be used as pigments for optical plastics. The color of the resulting nanocomposites is light-fast and intensive; in addition, these materials are perfectly transparent, since the cluster size is much lower than light wavelength. Gold, silver, and copper can be used for color filter application. Also, UV absorbers can be made, for example, by using Pd clusters. The plasmon surface absorption frequency is modulated by making intermetallic particles (e.g., Pd/Ag, Au/Ag) of adequate composition.

Polymeric films containing uniaxially oriented pearl-necklace type of nanoparticle arrays exhibit a polarization-dependent and tunable color. The color of these systems is very bright and can change, strongly modifying the light polarization direction. These materials are obtained by dispersing metal nanoparticles in polymeric thin films and subsequently reorganizing the dispersed phase into pearl-necklace arrays by solid-state drawing at a temperature below the polymer melting point. The formation of these arrays in the films is the cause of a strong polarization-direction-dependent color that can be used in the fabrication of liquid-crystal color display and special electrooptical devices.

Surface plasmon resonance has been used to produce a wide variety of optical sensors—that is, systems that are able to change their color in the presence of specific analytes. These devices can be used as sensors for immunoassay, gas, and liquid.

Metals are characterized by ultrahigh/low refractive indices and therefore can be used to modify the refractive index of optical plastics. Ultrahigh/low refractive index optical nanocomposites can be used in the waveguide technology (e.g., planar waveguides and optical fibers).

Plastics doped by atomic clusters of ferromagnetic metals show magneto-optical properties (i.e., when subject to a strong magnetic field, they can rotate the vibration plane of a plane-polarized light), and therefore they can be used as Faraday rotators. These devices have a number of important optical applications (e.g., magneto-optic modulators, optical isolators, optical shutters, etc.).

Nano-sized metals (e.g., gold, silver) have attracted much interest because of the nonlinear optical polarizability, which is caused by the quantum con-

finement of the metal electron cloud. When irradiated with light above a certain threshold power, the optical polarizability deviates from the usual linear dependence on that power. By incorporating these particles into a clear polymeric matrix, nonlinear optical devices can be made in a readily processable form. These materials are used to prepare a number of devices for photonics and electrooptics.

Finally, polymer-embedding represents a simple but effective way to use mesoscopic properties of nano-sized metals. A large variety of advanced functional devices can be based on this simple material class. In the last few years, a number of pioneering techniques have been developed for preparing metal–polymer nanocomposite materials. In particular, the *in situ* techniques based on the thermolysis of special organic metal precursors seems to be a very promising approach, principally for the possibility to produce metal–polymer nanocomposites on a large scale by techniques already available for thermoplastic polymer hot-processing.

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PHYSICAL AND CHEMICAL PROPERTIES OF NANO-SIZED METAL PARTICLES

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1. INTRODUCTION

A nanocluster is a tiny chunk of the bulk measuring a few nanometers with a finite number of atoms in it. Nano-sized metals with sizes in the range of 1–50 nm are considered important and are obtainable as sols—a dispersion of a solid in a liquid. Metal sols possess fascinating colors and have long been used as dyes and catalysts. That such dyes indeed consist of tiny metal chunks was established as early as 1857 by Faraday [1, 2]. Modern techniques of synthesis enable one to obtain sols of metals that can be dried and redissolved like water colors. The nano-sized clusters display a remarkable tendency to remain single-crystalline and hence are also called nanocrystals. In addition, nanocrystals possess a high surface area: A great fraction of atoms in a nanocrystal is on its surface [3].

An added dimension to research on nanocrystals is their size-dependent properties. The electronic, magnetic, and optical properties of a nanocrystal depend on its size [3]. In small nanocrystals, the electronic energy levels are