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Historical Perspective

Noble metal nanoparticles embedding into polymeric materials: From fundamentals to applications

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ABSTRACT

This review covers some key concepts related to embedding of the noble metal nanoparticles in polymer surfaces. The metal nanoparticles embedded into the polymer matrix can provide high-performance novel materials that find applications in modern nanotechnology. In particular, the origin of various processes that drive the embedding phenomenon, growth of the nanostructure at the surface, factors affecting the embedding including role of surface, interface energies and thermodynamic driving forces with emphasis on the fundamental and technological applications, under different conditions (annealing and ion beams) have been discussed. In addition to the conventional thermal process for embedding which includes the measure of fundamental polymer surface properties with relevant probing techniques, this review discusses the recent advances carried out in the understanding of embedding phenomenon starting from thin metal films to growth of the nanoparticles and embedded nanostructures using novel ion beam techniques.

Contents

1. Introduction

Nanoparticles (NPs) have fascinated researchers for over many decades and are now become a backbone of modern technology. NPs are promising research materials because of their potential applications in nanotechnology. The concept of nanotechnology was introduced by R. Feynman in 1959 [1] and later described by Taniguchi [2] in 1974. Since then, extensive research has been carried out in this field and realized that this category of nanomaterials has large potentials to make a significant impact to the human being and to the development of the society. Nanotechnology is a subtle aspect of science and engineering field refers to materials having dimensions in the order of 100th of nm or less [3]. Today, nanotechnology is a broad interdisciplinary area of research, development and is being extremely used by the industry which has

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been growing rapidly worldwide because of potential application in field of biomedical [4,5], electronics [6,7] and optical devices [8–10] etc.

In recent years, noble metal NPs have been embraced by the researchers and industrial sectors for both fundamental research and industrial applications. An important factor that attracts to research community is their optical, magnetic, electronic, and catalytic properties that are gaining commercial applications. In spite of these enhanced useful properties at a nanoscale level, when these NPs are embedded in a matrix such as a polymer, they exhibit exceptional physical properties due to quantum size effects [3,11]. Nanocomposite materials composed of these metal NPs embedded in a polymeric matrix are highly promising for a variety of technological applications because of the synergistic properties of their constituents [12–14]. Embedding noble metal NPs into polymeric materials to study and improve material properties has been fascinating in the last few decades. From a technological point of view, it is useful to embed the noble metal NPs in thin polymer films for the metallization of the polymer and for their optical and nonlinear applications [13–15]. These materials based on noble metals such as Ag and Au NPs exhibit unique optical properties that arise from localized surface plasmon resonance (LSPR) in nanodimensional structures that access a very large range of wave vectors over a narrow frequency band [9,10,13,14]. These NPs in a dielectric matrix show interesting SPR absorption usually observed in the visible region and that is due to their coherent oscillation of conduction band electrons when excited by electromagnetic radiation [9]. For example, optical absorption of solar cell is found to be enhanced by embedding noble AgNPs in the active layer [16]. Also, composite thin films embedded with NPs have demonstrated improved mechanical properties [17]. On the other hand, embedding noble metal NPs in a polymer has developed as a new probe to study the dynamic properties of the polymer surfaces near the glass transition under thermal annealing [18–20] as well as to study various surface phenomenon such as ion-interaction to the surfaces and induced modifications for embedding into the polymeric substrates [21,22], which are also of fundamental and technological interest.

In order to realize these useful properties of noble metal NPs for several applications, gaining fundamental understanding and probing of surface properties, a number of methods were used to embed metal NPs in polymer substrates such as vacuum deposition on viscous polymers, plasma polymerization combined with metal evaporation [23, 24], chemical synthesis in organic solvent [25], co-sputtering of metal and polymer [14,26–28], vapor-phase co-evaporation [29–32] etc. Other methods include heating of polymer substrates with supported metal NPs on the surface [33], metal ion implantation in polymer films [13], laser irradiation [34], and ion beam irradiation [35,36] of metal NPs on polymer surfaces. A wide range of methods for the fabrication of nanocomposites consisting of embedded metal nanoparticle by in situ grown metal nanoparticle in polymer, have been reported in recent review articles [37,38] and also discussed in a book by Heilmann [11]. Most of the literatures including review articles discuss about the methods of fabrication of embedded NPs and their enhanced properties in nanocomposites materials when incorporated within the polymer matrix. In addition to the technological importance of thin metal–polymer nanocomposites films, it is also of equal importance with point of fundamental interest that how NPs interact with polymer surfaces and become embedded into the polymer surfaces, and how embedding occurs to control the surface properties precisely at nanoscale level etc. Polymer nanocomposite thin films are model systems for understanding fundamental properties related to the materials, physical/chemical process that drives the embedding phenomenology and exploring fundamental principles that govern embedding of NPs into the polymer surfaces [33,36].

In this review article, in particular, metal–polymer interface, growth of the nanostructures at the surface/interface, embedding of noble metal NPs, origins of various processes that drive the embedding phenomenon including role of surface and interface, thermodynamic driving forces with emphasis on the fundamental and technological applications, have been discussed. In addition to the conventional thermal process, this review attempts to deal with a new aspect of novel ion beam techniques for embedding noble metal NPs in a polymer matrix and understanding of the embedding phenomenon starting from thin metal films to the growth of NPs at the surface and then embedded into the surface. For instance, the first section of this review article deals with the growth of NPs, their physics and chemistry on the polymer surfaces and interface formation. In the next section, the thermodynamic driving forces, responsible for embedding of nanoparticles, are discussed in brief with emphasis on surface and interface energies of the systems. The experimental works carried out in literature on embedding of noble metal NPs to probe polymer surface properties under conventional thermal processes have been reviewed in the next section. In the next section, embedding noble metal NPs have been reviewed under the influence of ion beam processes such as ion irradiation/mixing, ion implantation including ion interaction with solid materials with ion induced modifications in polymeric materials also receive detailed consideration. Most of the work which has been reviewed in this article is on noble metal NPs and polymer systems including some important discussion on other systems such as noble metal NPs/Silica systems. In the final section, we have discussed the future aspects of using these materials, techniques and conclude the review.

2. Noble metal NPs on polymer surfaces: Methods and interface chemistry/physics

Applications of metallized polymers in microelectronics and photonic devices have stimulated research of metal–polymer systems and their interaction at the interfaces for the development and better performance of the devices [39]. The various properties such as mechanical and electric properties of their interfaces are strongly affected by the degree of metal–polymer interdiffusion and intermixing; therefore the study of interfacial characteristics of metal and polymer under adverse conditions (annealing and irradiation) has significant importance both fundamentally and technologically [39–43]. Diffusion of metal in polymers affects the structure and formation of metal–polymer interface leading to a metal–polymer composite layer.

The study of thin polymer films embedded with metal NPs is a fascinating and active area in nanotechnology research. Most of the studies related to this particular area are motivated by advances in nanotechnology and outcome of such studies is the development of technologically important systems at a nanoscale. To understand these metal/polymer system, and embedding process, the first step is to understand the chemistry/physics of the interface including the properties of the materials at the nanoscale level because properties of the confined materials is always different from their bulk properties [44]. Metal NPs on the top of polymer surfaces play an important role in the potential use of polymer in the modern nanotechnology because of their unique electrical, mechanical, optical, antimicrobial properties which can be tuned by controlling their size, shape as well as the surface functionality of the both NPs and polymers [33,45].

To create such functional systems, with NPs positioned at the top of the polymer surfaces, most widely used methods are evaporation [7,46,47], thermal decomposition of organometalic precursors, and NPs suspended directly from the solution [33], sputtering followed by annealing [41–43]. For diffusion of Au NPs taken from the dilute aqueous suspension to the surface of poly(2-vinylpyr-idine) (PVP), Shull et al. [48] developed a model polymer–metal composite system to study the fundamental properties of Au metal NPs dispersion in polymer surface and found that diffusion process is coupled with bulk viscosity of the polymer.

The interface formation, growth of noble metal NPs and thin films (Ag, Au, Cu), control of size, their distribution on the various polymer surfaces and diffusion have been studied in detail by many groups [47,49–57]. Svorcik and group [42,58–61] have broadly studied the