



Thermally induced tuning of SPR of metal-fullerene Ag(26%)-C₇₀ nanocomposite



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ABSTRACT

A bi-functional nanocomposite thin film containing Ag nanoparticles embedded in fullerene C₇₀ is synthesized by thermal co-evaporation technique. Tuning of plasmonic resonance of Ag-C₇₀ nanocomposite is obtained by annealing the nanocomposite thin film at different temperatures from 80 to 300 °C for 30 min. The optical and structural properties of nanocomposite thin film with respect to high temperature are studied by UV–visible absorption spectroscopy and X-ray diffraction. Transmission electron microscopy is performed to investigate the temperature dependent size evolution of Ag nanoparticles in fullerene C₇₀ matrix. Growth of Ag nanoparticles is observed with increasing temperature above 200 °C due to enhanced diffusion of Ag in fullerene C₇₀ and Ostwald ripening. The optical and structural properties of metal-fullerene nanocomposite is not significantly affected upto a temperature of 150 °C, after that a progressive blue shift of ~27 nm in SPR wavelength is observed with increasing temperature. The tuning of SPR is ascribed to the thermal induced structural transformation of fullerene C₇₀ matrix into amorphous carbon and also to mutual polarization of the particles.

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1. Introduction

Nanocomposites materials are currently the most exciting and interesting area of research where the new materials with novel properties are being continuously developed. The nanocomposites in the form of thin films possess unique physical-chemical properties [1,2], enhanced mechanical [3,4], electronic [5,6], and magnetic [7] properties owing to the size effect [8–10]. These unique properties make them attractive for many industrial applications. A nanocomposite material is composed of two or more compounds which do not combine into a new one (Fig. 1). The properties of the nanocomposite material is not a simple combination of component properties and depend on the morphology and other characteristics of the component materials.

The selection of the nano-dimension filler component is first important step to form the nanocomposite. Metal nanoparticles are interesting material to be used as filler due to their remarkable optical and structural properties owing to their size effects and high surface to volume ratio. Nanoparticles of noble metal (Au, Ag and Cu) exhibit interesting optical properties which basically come from the collective

oscillations of conduction electrons in presence of electromagnetic radiation and is known as surface plasmon resonance (SPR) of metal nanoparticles. In general, the interaction of electromagnetic light with electronic cloud in metal nanoparticles comprises two different processes: (i) strong absorption and (ii) scattering. If particle size is small then absorption will dominate whereas major interaction will be in terms of scattering if particle size is large enough. These two processes are determined by the relative dimensions of the metal nanoparticle with respect to the wavelength of incident electromagnetic light. If the metal nanoparticles are much smaller than the wavelength of electromagnetic light, the field of the light is uniform across a particle and the electronic cloud moves in such a way that only dipole-type oscillations occur and a single peak in the SPR spectrum is obtained [11]. This oscillating electronic cloud induces polarization of the opposite direction in the matrix (where the nanoparticles are embedded) and ultimately affects the restoring force due to positive nuclei by reducing it to a lower value and thereby shifts the SPR value to a lower frequency. This change in SPR frequency due to change in the dielectric properties of matrix gives an idea to tune the SPR at a desired value by just altering the dielectric constant of the matrix using some perturbation after the film deposition [12]. The theoretical understanding of metallic nanoparticles and their interaction with light was provided by Gustav Mie, who

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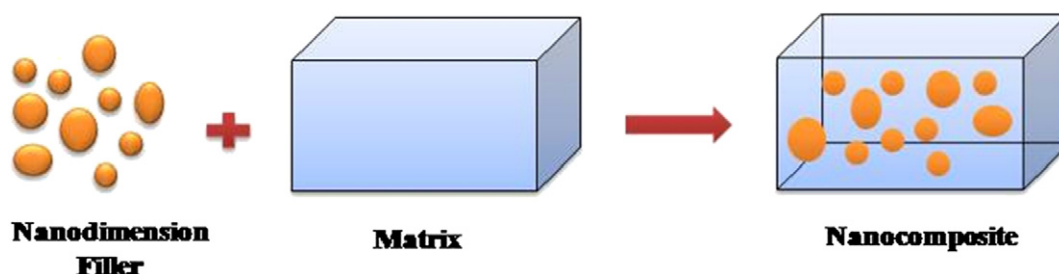


Fig. 1. Schematic of a typical nanocomposite.

solved the electromagnetic wave equations over an isolated spherical particle (without considering particle-particle interactions) and derived the extinction cross-section which can be approximated by the following formula called “dipolar approximation” [13]:

$$\sigma_{ext} = 9 \frac{\omega}{c} \varepsilon_m^{3/2} V_o \left[\frac{\varepsilon_2(\omega)}{\{\varepsilon_1(\omega) + 2\varepsilon_m\}^2 + \varepsilon_2^2(\omega)} \right] \quad (1)$$

Here σ_{ext} is the extinction cross-section of spherical nanoparticle, V_o is the volume fraction and ω is the applied optical frequency. $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is the dielectric constant of metal and $\varepsilon_m(\omega)$ = dielectric constant of embedding matrix. The above equation shows that the extinction cross-section depends on the size of the particles and dielectric constant of the host matrix (ε_m). Moreover when the volume fraction of the particles exceeds a few percent to the threshold, one must take into account their mutual polarization using an effective medium model such as Maxwell-Garnett theory.

Second step to form a nanocomposite is to choose the proper material for the matrix in which nanoparticles are embedded. In order to make the nanocomposite a bi-functional material, fullerenes are appropriate materials to be used as matrix. Fullerene C_{60} and C_{70} , both possess unique properties due to their size, electron affinity, high reactivity and bio-compatibility. Fullerene C_{70} is more appropriate with respect to the SPR of nanoparticles due to its high refractive index compared to fullerene C_{60} , but at the same time, the structure of C_{70} molecule is more complex than that of C_{60} . The C_{70} molecule has an ellipsoidal shape consisting of 25 hexagons and 12 pentagons [14]. The overall height of the relaxed C_{70} molecule is ~ 7.80 Å and the diameter of the equator is ~ 6.94 Å [15]. Regarding its crystal structure, it has been reported in literature that if fullerene C_{70} is prepared by sublimation route, it takes the fcc structure at room temperature [16]. On the other hand, if fullerene C_{70} is prepared by a solution route, it takes hcp structure at room temperature [17].

Fullerene C_{70} is a suitable material to host Ag nanoparticles and to form excellent nanocomposite due to following reasons: (i) Fullerene is a functional material having applications in various fields such as electronic devices, memory devices, catalysis, coatings, and hydrogen storage and especially in biology [18] and by embedding noble metal nanoparticles in fullerene C_{70} , the properties of metal nanoparticles as well as those of fullerenes can be simultaneously used, which makes this nanocomposite bi-functional, (ii) The primary role of a matrix to embed nanoparticles is to hold them and to prevent their agglomeration by Vander Waals forces and thus it gives stability to nanoparticles. Noble metals are chemically inert to carbon at ambient conditions and high cohesive energy of noble metals (3.48, 2.93 and 3.81 eV for Cu, Ag and Au respectively) [19] further leads to the nanoparticles separated from carbon phase, (iii) The interest to incorporate noble metal nanoparticles in fullerene matrix also comes from the tunability of SPR of these nanocomposite materials. A change in the dielectric constant/refractive index of the surrounding medium causes a shift in the resonance wavelength of nanoparticles as accounted by Eq. 1. It has been shown in literature [20] that the capability of tuning of SPR wavelength

by varying the metal concentration can be effectively enhanced by embedding the nanoparticles in a matrix of high refractive index. Fullerenes C_{70} , due to its high refractive index (~ 2.3 respectively) [21], is suitable in this respect, (iv) fullerene and its derivatives are excellent electron acceptor materials which are being used extensively in the polymer-fullerene bulk heterojunction organic solar cell. By embedding Ag nanoparticles in the active layer of the organic solar cell in term of metal-fullerene nanocomposite, the power conversion efficiency of the cell may be enhanced due to its strong absorption through plasmonic resonance, (v) with the thermal annealing, fullerene is transforming into amorphous carbon which is conducting and therefore the nanocomposite material may play the role of electrodes in various devices.

In the present study, thermal induced optical and structural transformations of metal-fullerene nanocomposite are investigated. The effect of ion bombardment on metal-fullerene nanocomposite has also been investigated by our group using ion beam techniques where by varying the ion fluence, SPR wavelength can be tuned to a desired position [22,23]. To get a control on the SPR position in terms of tuning of SPR frequency is important as it can greatly increase the number of applications based on SPR of nanocomposite, for example in surface-enhanced Raman spectroscopy where the excitation frequency must overlap with the SPR frequency [24] and also for the nonlinear optical properties of these metal nanoparticles where a large intensity dependent refractive index [24,25] is required to use these materials for optical switching and limiting devices [26].

Annealing is the simplest and cost-effective way for creating favorable modifications in properties of metal based nanocomposite thin films. In case of metal-fullerene nanocomposites, thermal treatment of the nanocomposite thin films results in gradual transformation of fullerene into amorphous carbon with a much lower refractive index and simultaneously, the metal nanoparticles generally grow in size with temperature with a possibility of mutual polarization in case of large metal content. As per the Mie theory, a decrease in the refractive index generally gives a blue shift to the SPR band whereas increase in size of metal nanoparticles gives a red shift to the SPR band. In the present study, the annealing of metal-fullerene nanocomposite is investigated keeping in mind the following two objectives: (i) The metal-fullerene nanocomposite is a very interesting system with respect to its annealing as it gives the possibility of both red and blue shift of SPR band in the same system which is very important for the theoretical understanding of plasmonic properties of metal nanoclusters where the simultaneous change of metal and matrix can be studied and modeled. This system is even more interesting as here matrix is also absorbing. (ii) The most emerging application of metal-fullerene nanocomposites is in organic solar cells. The fullerene derivative is being used in active layer and its absorption can be enhanced by incorporating noble metal nanoparticles in it. This can tend to enhance the overall efficiency of the device. During the fabrication of the device, the active layer is formed by the dissolution of two material in a common solvent. After the spin casting of active layer, annealing has to be performed to evaporate the solvent to avoid its unwanted effects. The annealing study of metal-fullerene nanocomposite is helpful to set a safe limit on the temperature for the evaporation of solvent in the active layer without

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