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Amorphization of polymer matrix with nanoparticle formation in spin coated PEI/Ag nanocomposites

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The present work reports the amorphization of polymer matrix with the nanocrystals formation in in-situ synthesized PEI/Ag nanocomposite films, where polyethyleneimine acts both as the reducing and stabilizing agent for the Ag nanoparticles. The fading of the diffraction halo characteristic of polymer along with the growth of cubic Ag phase in these nanocomposites has been observed from the x-ray diffraction studies. The intensity and position of the surface plasmon resonance (SPR) band strongly depends on the Ag salt concentration. The size of the nanoparticles was calculated using the Mie's theory and depends on the Ag content in these nanocomposites. The PEI/Ag films exhibits two luminescence bands (326 and 357 nm for sample A6) with small change in peak position with the Ag content. The optical gap and tailing parameter were also calculated for the discussion of the structure-property relationship in the nanocomposite films.

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1. Introduction

The study of polymer nanocomposites has generated intense research activity because of the absorption or emission properties of metallic and semiconductor nanocrystals hosted in the polymer components, have probable applications in optoelectronics and photonics [1, 2]. Among the wide range of hybrid nanocomposites, metal-polymer nanocomposites have been the focus of much work as noble metal nanocrystals exhibit surface plasmon resonance (SPR) and surface enhanced Raman scattering [3]. The enhancement in the nonlinear optical properties in Ag/PMMA nanocomposites shows the promise for practical use in all optical devices [4]. The increase in the concentration of Ag nanopartilces has resulted in the blue shift in the SPR band in PVdF/Ag nanocomposites along with α- to β-phase transformation of the host polymer [5]. The influence of annealing time and polymer/Ag ratio on the optical properties of the nanocomposites by spectroscopic ellipsometry and the localized absorption near the 420 nm (SPR band) has also been reported [6]. The decrease in the optical gap with increased room temperature conductivity has been ascribed due to the formation of charge transfer complexes in the sol-gel prepared nano-Ag and PVA nanocomposites [7]. The generation of silver nanoparticles in PVA matrix by reduction of silver ion with PVA molecules forms the Ag crystals (fcc structure) with average crystallite size 20 nm yields SPR single peak at 433 nm [8]. In general, the formation of SPR band is influenced by the size, shape, morphology, structure, surface chemistry and surrounding environment of the nanocrystals [9, 10]. These can be formed in liquid, solid state chemical reduction method of the metallic salt and their properties depends upon nature, property of the host/reducing reagents and the synthesis conditions, as it influences the nucleation/growth of nanoparticles as well as stabilizing effect for the particles [11-13]. The concentration of the metal salt and nature of the host polymer are important parameters to control the properties of these nanocomposites. Therefore, the present work reports the detailed study of the effect of metal salt concentration on the optical properties of in-situ synthesized silver nanoparticles in PEI matrix.

2. Experimental details

A simple one step reaction of $AgNO_3$ with PEI molecules is used to prepare Ag-nanoparticals embedded in part of the PEI molecules. In a typical reaction, 4 wt. % polyethyleneimine (PEI) was dissolved in cyclohexanone. Because of the reduced solubility of $AgNO_3$ in cyclohexanone, it was dissolved in ethyl alcohol and then mixed with polymer solution in 1:1 ratio. The resulting solution was spin coated on glass/quartz substrates at 1500 rpm for one minutes, dried and annealed at 393 K for 10 min on the hot plate. Similarly thin films of Ag-PEI with varying concentration of silver 0.02, 0.05, 0.08, 0.10, 0.15 and 0.2 M (named A1, A2, A3, A4, A5 and A6 respectively) were prepared. The amorphous/crystalline nature of these samples was studied at grazing incidence (2.5^o) by using x-ray diffractometer (Model D8 Focus, Bruker, Germany) using Cu-k_α radiation. The optical absorption of the composite films was studied by using UV-Vis spectrophotometer (lambda 35, PerkinElmer, USA) and emission spectra at 270 nm excitation energy was measured by using fluorescence spectrophotometer (LS 45, Perkin Elmer, USA).

3. Results and discussion

Fig. 1 shows the x-ray diffraction pattern for the annealed PEI/Ag nanocomposite films. It consists of three diffraction peaks, the first centered at 11.2° characteristic of the polymer, the second one centered at 23.4° due to glass substrate and the third peak centered at 38.3° for the synthesized nanocomposite films. The values of the wave vector (q-value) and full width at half maximum (fwhm) for the first peak are summarized in Table 1. The small variation in both these parameters has been observed, while further increase in Ag content results in the disappearing of this halo. In general, narrow diffraction peaks are associated with a good degree of crystallinity (i.e. full width at half maximum, fwhm ≈0.2), and broader ones for their semi-crystalline/amorphous behavior (fwhm≥1) [14]. Therefore, the increase in the Ag content modifies the polymer network to form of amorphous like PEI in this composite system. Generally, the addition of nano-Ag in polymers favors the growth of newer phase or improvement in the crystalline structure of the polymer network [5, 7]. However, these results suggest that the ion movement for the in-situ growth of nano-Ag modifies the polymer network for favoring its amorphous like form in this nanocomposite system. The third peak has been assigned to the (111) planes for the fcc Ag nanocrystals formed (d-spacing= 2.35 Å, fwhm= 0.0203 and particle size =7.14 nm for A6 sample) due to the reduction of Ag salt in the polymer matrix.

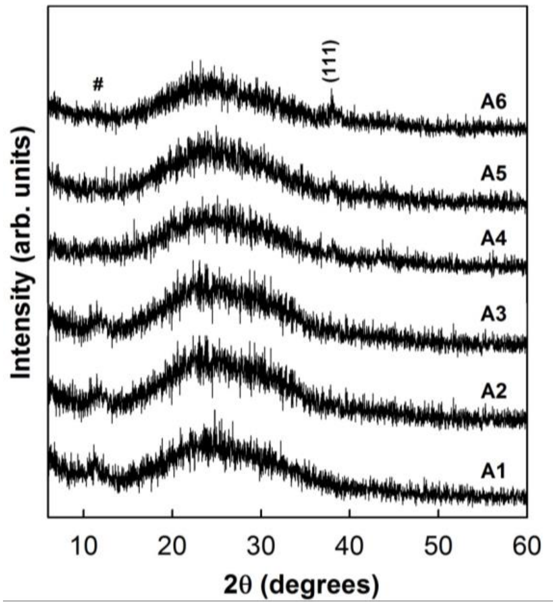

Fig. 1. X-ray diffractions patterns for the PEI/Ag nanocomposite films. The symbol "#" shows the crystallization of the polymer and the (111) plane for the cubic Ag nanoparticles.

Table 1. The calculated values of wave vector (q-value), fwhm (β_{XRD}), SPR peak (λ_{SPR}), fwhm ($\Delta w_{1/2}$), particle size (d), optical gap (E_g), tailing parameter (B^{-1}) and luminescence peaks (I & II) with Ag concentration in Ag/PEI nanocomposite films.

S.No.	Ag (mol)	q-value (nm^{-1})	β_{XRD} (rad)	λ_{SPR} (nm)	$\Delta w_{1/2}$ (nm)	d (nm)	E_g (eV)	B^{-1} (*m* eVcm)	PL-1 (nm)	PL-2 (nm)
A1	0.02	8.06	0.037	430.5	56.8	8.4	4.57	51.1	322	338
A2	0.05	8.29	0.038	424.6	56.5	8.3	4.51	54.8	323	341
A3	0.08	8.29	0.038	420.1	54.1	8.0	4.43	56.1	323	343
A4	0.10	8.11	0.039	422.3	73.2	10.8	4.22	59.4	324	353
A5	0.15	------	-------	422.3	50.7	7.5	4.31	59.1	324	354
A6	0.20	------	------	422.3	42.6	6.3	4.52	54.0	326	357

Fig. 2 shows the absorption spectrum of the PEI/Ag nanocomposite films. For sample A1 (0.02 N Ag concentration), the broad and asymmetric single peak at wavelength 429 nm and well-defined single peak has been observed for other samples. The peak position (λ_{SPR}) and fwhm (β_{SPR}) for the SPR band are summarized in Table 1. The gradual blue shift in the peak position up to A3 sample followed by the minute red shift along with the narrowing of the bandwidths of the SPR band has been observed. Similar results have been reported in the limit of the smaller particle sizes (2-20nm) observed for colloidal solutions [2]. Further, the mean size of Ag particles embedded in the polymer matrix has been estimated from the analysis of absorption spectra using the Mie-Drude theory according to the relation [15, 16]:

$$d = \frac{v_f}{\Delta w_{1/2}}$$

where $\Delta w_{1/2}$ is the full width at half maximum (FWHM) of the SPR band in angular frequency, d the average particle size and v_f the Fermi velocity of an electron and 1.39×10^6 m/s for Ag. The calculated values of the mean size of the Ag particles in our samples (Table 1). It has been observed that the largest particles are formed for the sample A4 (10.8 nm) and smallest particles are formed for the A6 (6.3 nm) where the maximum metal salt concentration is used for the synthesis of composite films. The value of the crystal size (for A6) is in good agreement with that calculated form the diffraction data. Since the rate of reaction depends on the molar concentration of reactants i.e. the time evaluation of the number of nuclei determining both the nucleation/growth process and thus forms smallest particles. As the size, density and nature of particles has major contributions for forming the SPR band, the increased density of the smaller particles may result in the decrease in the neighboring distance of particles and modifies the condition of the surface plasmon resonance band formation in these samples.

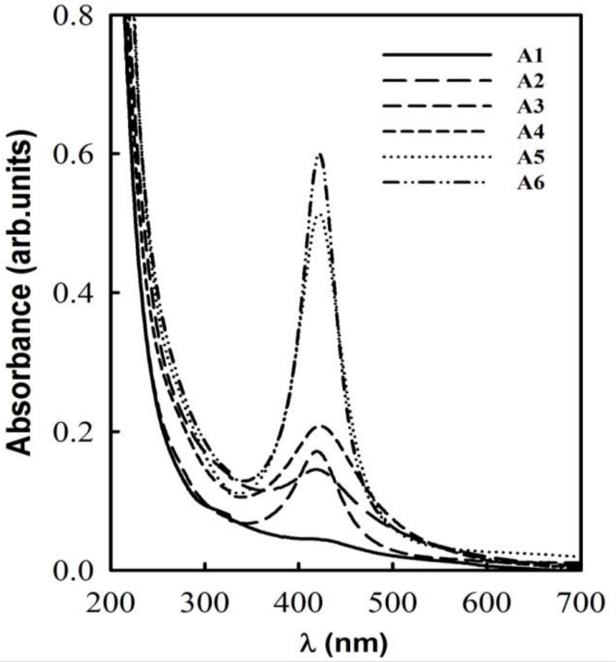

Fig. 2. The optical absorption spectrum for PEI/Ag nanocomposite films with different Ag concentration.

Fig. 3 shows the emission spectra of A4 and A6 samples at 270 nm excitation energy. The lesser luminescence signal may be due to the small density of nanoparticles embedded in composite films. It has been observed that fluorescence emission spectra of the Ag nanoparticles in Ag/PEI nanocomposites exhibit a complex behavior with two bands one narrow and one broad. Generally, the emission peak was centered near the interband absorption edge of the metal and therefore, was attributed to direct radiative recombination of the excited electrons in the sp-band with the holes in the d-band [17-19]. Similar, results has been observed for other samples and the peak values are summarized in Table 1. The minute red shift in the luminescence peak positions with the increase in Ag content has been observed in the present case.

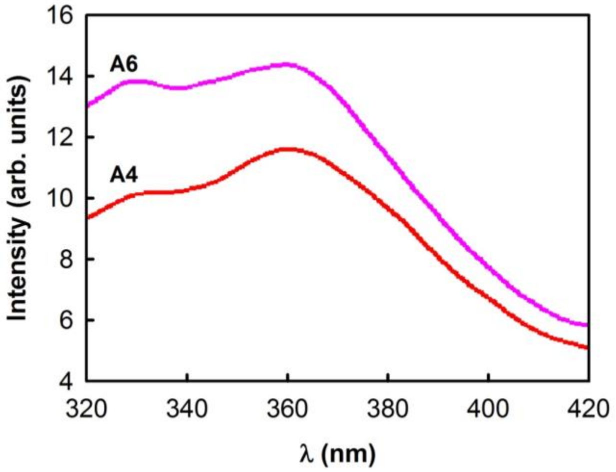

Fig. 3. Fluorescence emission spectra for PEI/Ag nanocomposite films at 270 nm excitation energy.

The formation of Ag nanocrystals in the polymer network also affects the optical absorption processes in PEI/Ag nanocomposite films. Its study also reveals the structural aspects of the in-situ formation of the nanocrystals, size and density in the polymer matrix for the nanocomposite films. The observed shift in the fundamental absorption edge can be correlated with the optical band gap (E_g) by Tauc's expression [20]: $(\alpha h\nu)^{1/2} = B\ (h\nu - E_g)$, where, α is the absorption coefficient corresponding to the fundamental absorption edge, hν is the photon energy and B is the constant of proportionality. Fig. 4 shows the plot of $(\alpha h\nu)^{1/2}$ versus photon energy (hν) for all the samples. Table 1 summarize the values of the optical gap (E_g) and tailing parameter (B^{-1}) for the nanocomposite films. It is found that the value of optical gap, 4.42 eV (A1) decreases to 4.10 eV (A4) and further followed by an increase 4.30 eV (A6) for increased Ag contents. This variation in the optical gap has been accompanied with the inverse relationship with the tailing parameter and the particle size in the studied samples. The structural constrictions due to the embedded nanoparticles increases with their size and consequently, the rise in tailing parameter with the increase in the structural disorder or a decrease in the optical gap of the synthesised films and vice-versa. The change in the bonding order of polymer chains with nanoparticle formation i.e. the smaller particles have lesser alterations in the polymer structure as compared to the bigger particles and found to affect their optical behaviour as observed in the present case. Similarly, the decrease in the optical gap has been reported for the nanoparticle doped polymer films [7, 21].

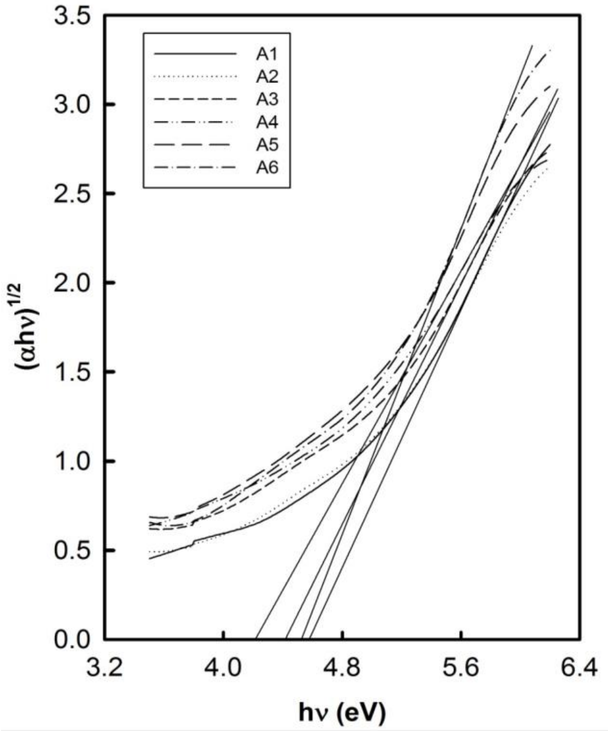

Fig. 4. Plots of $(\alpha E)^{1/2}$ versus photon energy ($h\nu$) for different composition of PEI/Ag films.

4. Conclusion

In-situ synthesis of Ag-PEI nanocomposites films were successfully synthesized by using solid state chemical reduction method with varying Ag concentration. The lessening of diffraction halo characteristic of the polymer at 11.2^o reveals the formation of amorphous polymer network with the formation of (111) of cubic Ag nanocrystals has been observed. The size of the nanoparticles was found to depend on the salt concentration as well as the found to influence the position and the intensity of the SPR band. The red shift in the position of two luminescence peaks has been observed at 270 nm excitation energy with the increase in Ag content. The inverse relationship between the optical gap and tailing parameter has also been observed for the synthesized nanocomposites. These results are explained using the variation in the particle size and density in the synthesized nanocomposites.

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