Effect of isopropyl alcohol for bimodal dispersion of silver nanoparticles inside polyaniline emeraldine base thin film

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The effects of isopropyl alcohol (IPA) on the dispersion of bi-modal silver nanoparticles inside polyaniline emeraldine base (Ag-PANIEB) as nanocomposite were investigated and discussed. Firstly, the bimodal Ag nanoparticles were synthesized with the help of precipitation method by semi-batch reactor and then ultrasonically blended inside the PANIEB matrix in the presence/absence of IPA followed by various characterization of Ag-PANIEB. It was observed that the bimodal dispersion of Ag nanoparticles inside PAIEB thin film was significantly improved in the presence of isopropyl alcohol (IPA). Such bimodal dispersion of Ag nanoparticles in the presence of IPA also enhances the electrical response of the Ag-PANIEB nanocomposite. A mechanism explaining the improvement in electrical response of bimodal Ag-PANIEB nanocomposite in the presence of IPA is proposed and discussed.

1. Introduction

Among conducting polymers, polyaniline has emerged as one of the most exceptional polymer due to its excellent environmental stability and electrical properties [1]. Polyaniline can be found in one of the following three common oxidized states: i) leucoemeraldine base, ii) emeraldine base, or iii) pernigraniline base [2], where polyaniline emeraldine base (PANIEB) can be regarded as the most useful form of polyaniline due to its high environmental stability and improved conductivity resulting from doping by either some suitable acid or nanoparticles [3-4]. For many electronic applications of conducting PANIEB such as conductive inks, conductive adhesives, and electromagnetic wave shields, heavy loading of Ag inside PANIEB matrix is required [5,6]. But due to the strong surface energy of Ag nanoparticles, these nanoparticles are agglomerated and degrade the electrical responses of PANIEB matrix. For the dispersion of Ag nanoparticles inside polymer, many types of surfactants are used, but still these surfactants degrade the electrical response of PANIEB matrix [7,8]. At the same time the bimodal dispersion (broadly speaking two average size dispersion of nanoparticles) significantly enhances the electrical response of many conducting polymer by improving the packing density of nanocomposite by removing voids and pores of polymer [9,10]. But unfortunately the even dispersion of bimodal nanoparticles

inside polymer is still a challenging task [11, 12].

In this study we observed that the dispersion of bimodal Ag nanoparticles inside polymer is significantly improved in the presence of isopropyl alcohol (IPA) without degrading the electrical response of Ag-PANIEB nanocomposite. Therefore, different characterization was carried out to investigate and discuss the effect of IPA on structural, electrical and optical properties of bimodal Ag-PANIEB nanocomposite.

2. Materials and experimental procedures

2.1 Materials

The following chemicals were purchased from various companies such as: Silver nitrate ($AgNO_3$, 99.9%, KOJIMA Co. Ltd.), Myristic acid ($C_{14}H_{28}O_2$, 97%, ACROSS), Sodium hydroxide (NaOH, 98%, SAMJUNG), Triethylamine ($C_6H_{15}N$, 98%, SAMJUNG), while PANIEB (Mwt ~ 50,000 gm/mole) and IPA (($CH3)_2CHOH$) were purchased from Sigma Aldrich. All these chemical were used as-received without any further purification.

2.2 Synthesis of Ag nanoparticles

For fabrication of bimodal Ag nanoparticles, the precipitation method by semi-batch reactor was used. For this method, 0.2 M $AgNO3$ solutions were taken in a

beaker and 0.2 M NaOH and 0.2M myristic acid solution were added into the beaker by micro-feed pump (MP-3, EYELA) in a controlled manner. The semi-batch system helps not only to control the size and shape, but also control the size dispersion of Ag nanoparticles due to its short nucleation and a slower reaction rate. After submission of myristic acid solution and NaOH, white color intermediate Ag-ligand precipitate called "Ag myristate" was obtained. The Ag myristate was immediately washed with the help of de-ionized water and filtered by quantitative paper and then it was dried at 50 ^{o}C in a vacuum oven for nearly 24 h. At final stage, Ag myristate was reduced by means of triethylamine (TEA) at ~80 ^{o}C for nearly 2 hours. Reduced Ag nanoparticles were cooled and centrifuged at 12,000 rpm for 5 min. The general information about the above semi-batch method for bimodal fabrication of Ag nanoparticles can be found in previously published results [13, 14].

2.3 Fabrication of nanocomposite

Nanocomposites were fabricated by an ex-situ preparation method in which already prepared Ag nanoparticles were used for nanocomposite. The 15% of PANIEB solution was mixed in IPA with conventional laboratory techniques. Ag nanoparticles were dispersed in PANIEB and PANIEB-IPA solution with Ag nanoparticles by 10% weight concentrations (with respect to PANIEB) by using ultrasound (Power Sonic 410) for ~30 minutes. For electrical characterization, 500 nm thin film of nanocomposite was successfully developed using a spin-coating method (MIDAS System: 1200–d) on the top of aluminum thin film as electrode.

2.4 Characterization

For external electrical connection, circular-shaped (diameter ~1 mm) metal electrodes were patterned by using thermal evaporator under a vacuum pressure on both aluminum and a PANIEB thin film based on a full Kelvin style (two electrodes on aluminum and two electrodes on PANIEB thin film, respectively). A collinear geometry was adopted for patterning the electrodes, i.e., equally spaced (~5 mm), in-line arrangement with other adjacent electrodes. In order to remove the IPA and other traces, the devices were annealed at 100 °C for more than two hours. A schematic cross-sectional view of the finished device is shown in Fig. 1.
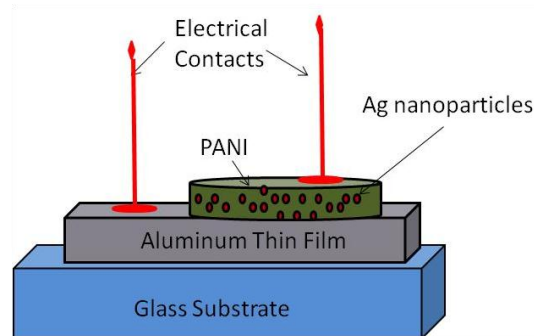

Fig. 1. A schematic cross-sectional view of bimodal Ag-PANIEB thin film deposited with a spin-coating method onto an aluminum thin film on a glass substrate with four electrodes used for electrical characterization. For simplicity, here only two electrodes are shown.

For other characterization, transmission electron micrographs were taken by JEOL (JEM 3010). An Optizen 2120 UV spectrophotometer was used to record the UV–vis absorption spectra. The X-ray diffraction was performed with the help of D/MAX 2000, Rigaku, Japan by using Cu Ka radiation. Current-voltage (*I-V*) characteristics of the thin films were measured in the dark using a four-point probe HP4145B parameter analyzer controlled by computer.

3. Results and discussion

3.1 Morphology of Ag nanoparticles

Morphology and dispersion of nanoparticles inside polymer play a very vital role to define the electrical responses of nanocomposite. Therefore, TEM micrographs were used to determine the morphology and dispersion of the bimodal Ag-PANIEB nanocomposites with and without IPA are shown in Fig. 2. In Fig. 2a, Ag-PANIEB nanocomposite where no IPA is used, Ag nanoparticles are coagulated inside PANIEB matrix; however the addition of IPA prevents the nanoparticles to form coagulation and great majority of the nanoparticles appear as individual particles rather than aggregates inside the PANIEB matrix as shown in Fig. 2b. Close-view of Ag nanoparticles clearly demonstrates that nanoparticles are bimodal distributed with spherical shape and smooth surface morphology and each have some crystalline domains (Fig. 2c). Similarly, It is also observed that the Ag nanoparticles exhibited bimodal dispersion with a relatively large density (>50% of total Ag concentration) of particles at smaller sizes (major mode) and relatively smaller Ag nanoparticles density (~ 30%) at the larger sizes (minor mode) and are distributed throughout the film. Fig. 2d shows a histogram of major and minor modes with a broad size dispersion of Ag nanoparticles in which the dispersion of Ag nanoparticles was somehow clarified in a PANIEB matrix. The average particle sizes in the major and minor modes were approximately 20±5 nm and 75± 10 nm, respectively. The improved dispersion of the nanoparticles is due to the presence of IPA, which forms complex

organic layer on the silver nanoparticles with a binding energy greater than the room temperature thermal energy [see inset of Fig. 2d]. This layer causes the nanoparticles to modify their surface properties to avoid excessive agglomeration in the solution.
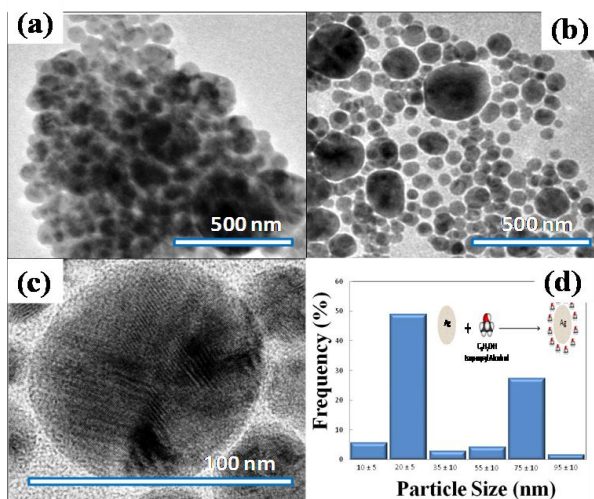

Fig. 2. TEM micrographs, a) shows sample with dispersion of Ag nanoparticles in the PANIEB matrix, without IPA, where Ag nanoparticles are coagulated, b) shows dispersion of Ag nanoparticles in the PANIEB matrix with IPA, where Ag nanoparticles dispersion is improved, c) shows TEM image of a single Ag nanoparticles inside PANIEB matrix, showing their spherical, smooth surfaces and multi-crystalline structure and as well as thin organic layer on their surfaces. d) A histogram showing the broad dispersion of Ag nanoparticles with major and minor modes of Ag nanoparticles using data from the TEM images which clarifies the bimodality of the Ag nanoparticles in the PANIEB matrix, inset of figure shows the attachment of IPA molecule on the surface of Ag nanoparticles to avoid coagulation inside PANIEB matrix
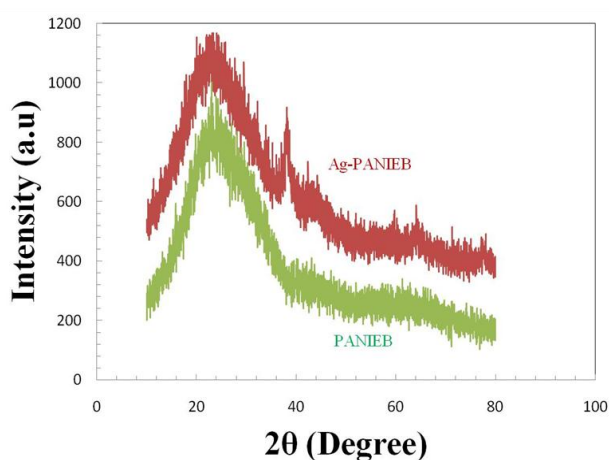

Fig. 3. XRD patterns of a) pristine PANIEB, and b) Ag-PANIEB Nanocomposite with IPA.

3.2 Morphology of conducting polymer

Just like the morphology of nanoparticles, the morphology of polymer also affects the electrical response of nanocomposite. To investigate the morphology of the polymer, the XRD patterns of the pristine PANIEB and Ag-PANIEB nanocomposites with IPA are presented in figure 3. Both XRD pattern shows the similar peaks except the peak associated with Ag nanoparticles and all peaks are in full agreement with the reported peaks for both Ag and Ag-PANIEB nanocomposite [15, 16]. The broader peak at 2θ of about $28.4°$ is related to the diffraction of amorphous PANIEB, and the other peak at $38.2°$ is associated with the diffraction of Ag particles. Apart from these peaks, several other weak peaks which are the characteristic peaks for the amorphous nature of polyaniline indicated a short range order in PANIEB probably induced by the presence of the IPA. The overall length of short-range-order (*L*) (or crystalline domain of PANIEB) can be extracted from the characteristic peak of a XRD profile with help of the Scherrer equation;

$$L = \frac{0.9\,\lambda}{\Delta(2\theta)\,Cos\,\theta} \tag{1}$$

where $\Delta(2\theta)$ is a full-width at half-maximum (FWHM) of the characteristics peak, 2θ the scattering angle of a X-ray associated with the characteristics peak, and λ the wavelength of X-ray radiation used (CuKα, λ=1.5418 Å). The amorphous (noisy and broader) nature of a characteristic peak is reflected in the FWHM value (0.26 ± 0.02 radian); hence, the short-range-order is calculated to 5.5 ± 0.4 nm [17], and negligibly degraded in the presence of bimodal nanoparticles. Similarly it is further observed from the XRD patterns that the high intensity of the Ag associated peaks is due to heavy loading of both Ag nanoparticles in the PANIEB matrix. It is further observed that the morphology of PANIEB is negligibly degraded in the presence of IPA and Ag nanoparticles for Ag-PANIEB nanocomposite. Here XRD pattern of Ag-PANIEB without IPA is not shown due to very similar response as Ag-PANIEB with IPA. It clearly demonstrates that IPA does not play any significant role to alter the morphology of PANIEB.
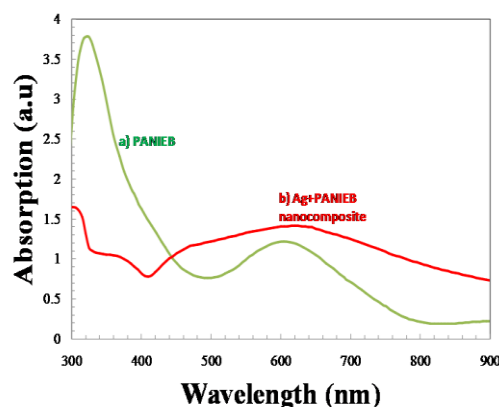

Fig. 4. Optical absorption spectra for a) PANIEB, and b) Ag-PANIEB (with or without IPA) nanocomposite.

3.3 Optical response of nanocomposite

Uv-visible spectroscopy is another important tool to investigate the electronic properties of conducting polymer based nanocomposite. Generally IPA does not absorb optical spectra at uv-visible range, therefore the IPA does not change the uv-visible spectra of Ag-PANIEB nanocomposite. Here both PANIEB and Ag-PANIEB nanocomposite were characterized by UV-visible spectroscopy as shown in Fig. 4. From spectra, two distinct peaks are observed at about ~320 nm and ~610 nm. The peak at ~320 nm may correspond to the $\pi - \pi^*$ transition of benzene rings. Another peak within the range of ~610 nm may correspond to the radial cation (semiquinone structure) of PANIEB. A comparative study of the absorption spectra of PANIEB and Ag-PANIEB nanocomposites shows that the peak at around 320 nm is reasonably suppressed and the peak at around ~610 nm is significantly enhanced and slightly shifted due to the presence of bimodal Ag nanoparticles in the nanocomposite [18]. The significantly enhancement and shifting of the peak at ~610 is may be due to the heavy loading of bimodal Ag nanoparticles.

3.4 Electrical response of nanocomposite

Using four-point probe semiconductor parameter analyzer, the *I-V* characteristics of the samples is evaluated at room temperature. To determine the effect of IPA on the electrical response of nanocomposite, a thin film of Ag-PANIEB without IPA were deposited and characterized under similar environmental conditions. The *I-V* characteristics of thin films of a) PANIEB, b) Ag-PANIEB nanocomposite without IPA and c) Ag-PANIEB in the presence of IPA, shows linear, symmetric, and non-rectifying (ohmic) response for all samples, as shown in Fig. 5. In the presence of Ag concentration without IPA the sample (Ag-PANIEB without IPA) shows slightly improvements in electrical response compared with PANIEB thin film, may be due to the agglomeration and non uniform dispersion of Ag nanoparticles inside PANIEB matrix. While the conductivity of nanocomposite found higher in the presence of IPA. Although IPA evaporates during annealing process before electrical characterization, but may be the IPA improves the uniform dispersion and hence packaging density of the nanoparticles inside PANIEB during thin film fabrication process for high conductivity. The improvement in conductivity of Ag-PANIEB nanocomposite in the presence/absence of IPA can be qualitatively explain by a hopping mechanism, commonly reported for many organic/polymer materials [19-25]. According to the Mott theory for hopping mechanism, the transition rate (W_{ij}) of a charge carrier hopping from one localized state *i* to the other localized state *j* can be expressed as follows [26]

$$W_{ij} = v_0 \exp\left(-2\alpha R_{ij}\right) \exp\left(-\frac{\Delta E_{ij}}{K_b T}\right) \qquad (2)$$
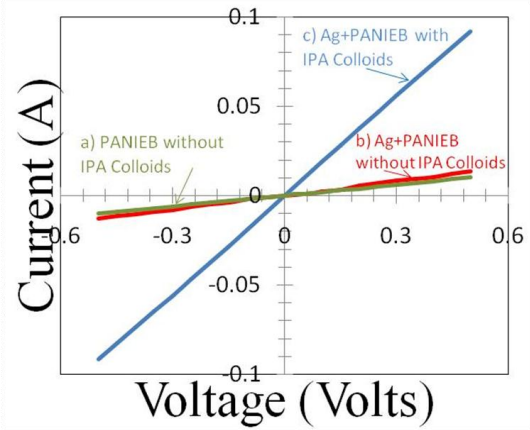

Fig. 5. Rectifying characteristics of a) pristine PANIEB thin film b) Ag-PANIEB nanocomposite thin film without IPA, and c) Ag-PANIEB nanocomposite thin film with IPA.
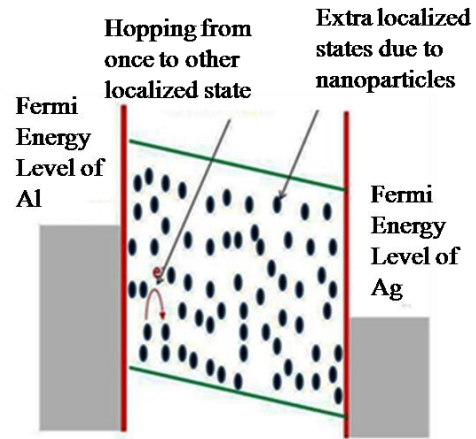

Fig. 6. Energy band diagram of Ag-PANIEB nanocomposites with their metal electrodes showing the additional localized states provided by the Ag nanoparticles, which enhance the hopping transport mechanism inside the PANIEB nanocomposite.

Here α is the inverse localization length, R_{ij} is the hopping distance, ΔE_{ij} is the energy difference between the two localized states, k_B is the Boltzmann constant, v_0 represents the number of hopping attempts per unit of time, and T is the temperature.

From the above equation, it can be noted that the hopping mechanism is significantly improved with lower hopping distance. The incorporation of Ag nanoparticles inside the PANIEB matrix provides extra localized states and, hence reduces the average hopping distance for the carriers, as compared to the pure PANIEB matrix, see Fig. 6. If the bimodal Ag nanoparticles is evenly disperses inside the PANIEB matrix then the average hopping distance is considerably reduced due to further localized states, stem from high packing nanoparticles density for continuous path compared to the pure PANIEB matrix. In contrast, if nanoparticles are coagulated and not disperse uniformly then average hoping distance is not significantly improved compared to Pure PANIEB. As it is already discussed that IPA improves the dispersion of Ag

nanoparticles inside PANIEB, therefore, nanocomposite in the presence of IPA shows much higher conductivity compared to the Ag-PANIEB nanocomposite without IPA.

5. Conclusion

The effect of isopropyl alcohol (IPA) on the dispersion of bimodal silver nanoparticles inside polyaniline emeraldine base (Ag-PANIEB) as nanocomposite were investigated and discussed. The bimodal Ag nanoparticles were synthesized with the help of precipitation method by semi-batch reactor and then ultrasonically blended inside the PANIEB matrix. It is observed that the bimodal dispersion of Ag nanoparticles inside PAIEB thin film is significantly improved in the presence of IPA compared to the dispersion of bimodal Ag nanoparticles inside PANIEB without IPA. It is proposed that the improved dispersion of bimodal Ag nanoparticles reduces the average hopping distance by offering new localized states inside the PANIEB matrix. These new localized states provide continuous path for efficient charge transport and hence improve the overall electrical response of the nanocomposite in the presence of IPA. It is suggested that this study will extend the practical applications of bimodal Ag-PANIEB nanocomposites for different electronic applications.

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