Synthesis and Characterization of Silver/Polyvinilpirrolidone (Ag/PVP) Nanoparticles Using Gamma Irradiation Techniques

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In this paper, attempts have been made to synthesize silver (Ag)/Polyvinilpirrolidone (PVP) nanoparticles by ionizing radiation and at the same time overcoming some of the disadvantages previously reported by other methods such as impurities, solvent toxicity, size and distribution control and difficulty in their preparation that limits their commercialization potential. The use of an alternative method overcomes some unfavorable characteristics like long tedious and costly process, uncontrolled size and distribution. The advantages of radiation processing of the materials relative to other methods are: no metallic catalyst is required; gives pure product; no oxidizing or reducing agent is required; the process occurs at a liquid or/and solid-state condition; it is fast and inexpensive; and environmental friendly with controllable acquisitions. Ag/PVP nanoparticles were successfully prepared in one-step by γ-irradiation technique in an aqueous system at room temperature and under ambient pressure. The transmission of electron microscopy (TEM) of the as-prepared product particles ranged from 100 to around 8-nm depending on the irradiation dose value, which showed a good distribution with a controlled size as the dose was changed. The presence of PVP polymer was considered as an important reason that influenced the shape and distribution. The band gap energy was calculated from the UV-VIS absorption spectra. Thermal analysis TGA showed that the composite had a higher degradation temperature than the PVP alone. This result indicates that AgNO₃ can effectively dope PVP and enhance the optical and thermal properties. In addition, γ-irradiation is an effective technique for preparing inorganic/organic nanocomposites.

1. Introduction

The nanoscale metal particles such as silver and gold provide a very exciting research field because of their interesting optical, electronic, magnetic and catalytic properties. The metal nanoparticles, therefore, have potential uses in technological applications. Silver exhibits the highest electrical and thermal conductivities among all the metals[1].

Ag metal nanoparticle/organic polymer composites have attracted considerable interest in recent years because of the advantageous properties of metals and polymers built into them. Many methods have been developed for the fabrication of the metal/polymer nanocomposites. However, the major disadvantages in the preparation of polymer metal nanocomposites by some methods are the poor distribution of the inorganic nanoparticle size and the poor dispersion of the inorganic particles in the polymer host and the use of toxic material for reduction of metal. In these methods, the formations of the polymer matrix and inorganic nanoparticles are performed in two separated steps. Therefore, it is difficult to avoid both the phases of separation and the aggregation of small particles. In addition, a heat treatment or high pressure is necessary under such conditions, which makes the preparation procedure more complex and difficult.

Gamma-irradiation has been successfully used to prepare nanocrystalline and nanometer-size metal/polymer nanocomposites have been prepared with a one-step synthesis with γ-irradiation in aqueous solutions [2-5]. A possible mechanism of the formation of Ag nanoparticles by gamma irradiation system is proposed in Scheme 1. The color of the irradiated samples were changed from colorless (before irradiation) to yellow or golden yellow and to darker colors as the dose was increased. This result may be due to the reduction of AgNO₃ in Ag nanoparticles in PVP matrix that
acts as a binder or protective agent. This restricts the mobility of the Ag ions during chemical reaction, prevents aggregation among the Ag nanoparticles and limits the size of Ag nanoparticles [6,7]. Gamma irradiation offers many advantages for the preparation of metal nanoparticles. Large number of hydrated electrons produced during γ-ray irradiation can reduce the metal ions to zero valiant metal particles [8]. A summation made by [9,10] suggested that irradiations cause a chemical change in polymers, including cross linking, chain scission, formation of C=C, formation of alkyne groups, and depletion of heteroatoms (e.g. N, S or O). In addition, an extensive study done by [11] on polycarbonate via irradiation-induced changes confirmed that irradiation induces conductivity and enhances their thermal properties. The effect of irradiation using neutron, ion or e-beams on polycarbonate is primarily the chain scission.

In recent years, studies on the electrical and optical properties of polymers have attracted much attention in view of their application in optical devices. The optical properties of polymers can be suitably modified by the addition of dopants depending on their reactivity with the host matrix. Although some studies have reported charge carrier transport and optical properties of doped polymers, to the best of our knowledge no work is available on doped PVP. PVP is a potential material with very high dielectric strength. Furthermore, it has a good charge storage capacity and dopant-dependent optical properties. Since AgNO₃ is a fast conducting ion in a number of crystalline and amorphous materials, its incorporation within a polymeric system may be expected to enhance its electrical and optical performance.

The incorporation of inorganic/organic material is believed to remarkably improve a wide range of properties of the polymers due to the nanosized dispersion [12]. Among these properties, the enhancement of thermal property is one that has been observed in many polymer nanocomposites [13]. It was reported that incorporation of inorganic/organic material significantly elevates the glass transition temperature and the degradation temperature of the neat polymer [14-16]. In this paper, we extend the above γ-irradiation method to the synthesis of Ag/PVP nanocomposites in an aqueous solution. TEM observations showed that the Ag nanoparticles with smaller size and well distributed were obtained at higher dose. The UV-Vis spectra of the nanocomposite were also studied to calculate the optical band gap energy.

2. Materials and Methods

Silver nitrate (AgNO₃). Polyvinylpiperidone PVP Mw =10,000 (Aldrich), and other chemicals were used as received. Deionized water was prepared in the laboratory, Isopropyl alcohol (IPA) was used as a radical scavenger in all samples.

Ag/PVP nanoparticles have been synthesized by using γ-irradiation process. For this purpose, procedures were done in a clean room, with appropriate amount of AgNO₃ and PVP dissolved in de-ionized water separately (Scheme 1) and maintained under vigorous stirring until a homogeneous solution was obtained. The two solutions were then mixed under vigorous stirring for one hour in the presence of IPA. The initially homogeneous solution was bubbled with nitrogen for half an hour before it was irradiated. In order to study the effect of γ-irradiation on the mixture, five samples were sealed and sent to Gamma cell to be irradiated at different doses ranging from 10 to 50-kGy in a step of 10-kGy. It is important to note that the quantity of PVP, IPA and water were 0.5 gram, 5 ml and 50 ml, respectively, in all the samples. Moreover, the effect of AgNO₃ concentration was also studied as shown in Scheme1.

The mixture was prepared and stirred in a dark room at room temperature so as to prevent UV radiation present in the environment from reducing AgNO₃ into silver nanoparticles before the treatment with γ-radiation. The purified yellow or/dark golden precipitate was centrifuged and washed in deionized water and ethanol several times to be ready for examination through different instruments. It is important to mention the color of the Ag nanoparticles solution is yellow and becomes darker as the dose increases or/and as the concentration of AgNO₃ increases. This indicates a larger amount of reduction of AgNO₃ to Ag nanoparticles.
3. Results

3.1 The effect of gamma irradiation and AgNO₃ concentration on the morphology by TEM and STEM

In order to study the effect of irradiation dose on the reduction of AgNO₃ to Ag nanoparticles in PVP solution, TEM images at different doses were taken for Ag/PVP nanocomposites. The result reveals that a higher gamma dose will lead to a greater reduction of AgNO₃ to Ag nanoparticles in PVP solution and the formation of smaller particles is clear with better distribution.

The function of PVP in the Ag/PVP composites is not only as a binder but it also prevents the process of agglomeration of Ag nanoparticles [6, 8] and limits the diameter of the nanoparticles formed.

In this study, polymers were used because of the hydrophilic nature of PVP that protects the surface of the Ag nanoparticles. The average particle size of Ag/PVP at different doses with a fixed amount of 0.3 g of AgNO₃ was estimated to be ranging from around 6 nm at 50-kGy with the well distribution to about 100 nm at 10-kGy with irregular shapes (Figs. 1 and 2).
Moreover, the effect of the molar ratio of AgNO₃ to PVP was observed by STEM and TEM, which revealed that as AgNO₃ concentration is increased in the system, size increases with an irregular shape. The average particle size of Ag/PVP prepared at 40-kGy with different mass of AgNO₃ was estimated to be around 50 nm for that of 0.5 g of AgNO₃ with even distribution and needle shaped. In addition, 0.4 g of AgNO₃ was estimated to be smaller with similar shapes for both concentrations, as shown in Fig. 3 and Fig. 4, respectively.

This indicates that the diameters of nanomaterials can be controlled directly by the appropriate selection of parameters. In addition, nanomaterials obtained by our method all show similar ranges of diameters up to several nanometers. Different shapes and different composites can also be produced by gamma irradiation Ag/polystyrene nanorod and CdS/PVP quantum dots, which was prepared by our research group [5, 38]. The formation, size and distribution of Ag nanoparticles were controlled by varying the dose as shown in the TEM images satisfying our objectives.

3.2 The effect of gamma irradiation and AgNO₃ concentration on the optical band gap energy by using UV-Vis spectra

Figs. 5A and 5B show the UV–vis absorption spectra for different wt % of AgNO₃ (0.7, 1.5, 2.1, 2.9 and 3.6) and for different Gamma dose ranging from 10 to 50-kGy in a step of 10-kGy. All samples
of Ag/PVP nanoparticles were dispersed in the absolute ethanol and carried out by using the absolute ethanol as reference. The UV–Vis absorption spectra further indicates the formation of Ag nanoparticles via gamma irradiation. The characteristic peak of the Ag nanoparticles appears in the range of 400 to around 440 nm, depending on the value of gamma doses which is caused by surface plasmon resonance [17]. The surface plasmon phenomenon, i.e., cloud electromagnetic waves coupled with the CB electrons, shows the peak at 440 nm shifting to lower wavelength and indicating a decrease of grain sizes of Ag nanoparticles within the PVP solution following the reduction at higher doses (π→π* transition). It is well known that the surface plasmon resonance bands of metal nanoparticles are sensitive to their surrounding environment absorption of the electrons in the conduction bands of silver. Surface plasmon bands appearing in the visible region are characteristic of the noble metal nanoparticles. Surface plasmons are collective oscillations of free electrons at metallic surfaces.

![Fig.5: UV – vis absorption spectra for (A): different weight of (wt %) AgNO₃, and (B): different Gamma dose.](image)

The peak is seen in Fig. 5B, which shows that the plasmon absorption peak appeared around 430 nm for a sample prepared at 10-kGy and shifted to lower wavelength with the increase of the gamma dose influence, and subsequently reached around 410 nm for a sample prepared at 50-kGy. In addition, as shown in Fig. 5A, the peak is shifted to higher wavelength as AgNO₃ continents increase. Furthermore, there are two absorption peaks as shown in the above figures, where the weak one is at around 280 nm and the prominent one at around 415 nm. The absorption peak at 280 nm is associated with NO₃ compound, which increases with the dose influence due to the consumption of Ag⁺. The absorbance band at 415 nm is attributed to the surface plasmon resonance phenomenon of free electrons in the conduction bands of Ag nanoparticles. This result is in complete agreement for that Ag nanoparticles prepared by chemical reaction [18].

![Fig.6: Plot of absorbance vs. (A): Different concentration of AgNO₃, (B): Different Gamma dose (kGy).](image)

The intensity of these bands was increased as the dose and/or the AgNO₃ continents increased in the system indicating more reduction of AgNO₃ to Ag nanoparticles as shown in Figs. 6A and 6B, respectively.

The band gap of a material is defined as the energy distance between the valence and...
conduction bands (CB). The smaller the band gap, the more electrically conductive a material will be. Metals have small band gaps whereas insulators have larger band gaps, which explains why there are so few electrons found in their conduction bands. There is not sufficient energy to excite electrons from the valence band to the conduction band in the case of insulators. Semiconductors occupy a middle ground and have tractable band gaps, which when given enough thermal energy can excite electrons into the conduction band. One can also add dopants to polymers like cadmium sulfide quantum dots, silver nanoparticles that make a polymer behave more like a semiconductor or a conductor by introducing additional energy levels within the band gap. The organization of energy levels is quite different between nanomaterials and bulk materials in those nanomaterials have larger band gaps and consist of more discrete energy levels. This observation may be attributed to the various quantum confinement effects within nanoparticles whose sizes can be as small as only a few dozen atoms wide (couple of nanometers). Generally, the optical band gap energy in semiconductors is determined by plotting absorption coefficient $\alpha(v)$ as $(\alpha(v)\nu)^{1/m}$ vs. $\nu$, where $m$ represents the nature of the transition and $\nu$ the photon energy. In addition, $m$ may have different values, such as $\frac{1}{2}$, 2, $\frac{3}{2}$ or 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively.

Practically, at room temperature, the optical absorption spectra (UV-vis) measurement is in the wavelength region of 190–900 nm. This evaluation was done at 415 nm using Mott & Davis concept for the direct optical band gap energy for those samples prepared with 0.1 to 0.5 g of AgNO$_3$ in a step of 0.1 g (0.7 wt % to 3.6 wt %) in PVP at 30-kGy doses. Here the band gap energy may be determined from the extrapolation of the linear section of the curves to x-axis in which $(\alpha(v)\nu)^2 = 0$. This will give the band gap energies of the surface plasmon resonance absorption of electrons in the conduction bands of silver Ag nanoparticles induced by $\gamma$-irradiation at various dopant concentrations (AgNO$_3$), as shown in Fig. 7.

The band gap energy decreases following the AgNO$_3$ concentration from 2.71 eV at 0.7 wt % of AgNO$_3$ to 2.2 eV at 2.9 wt % of AgNO$_3$ and then shows an increase to 2.38 eV when the dopant concentration of AgNO$_3$ is increased to 3.6 wt % as presented in Fig. 7. In addition, the result showed a strong dependence on the concentration of the AgNO$_3$ dopant showing a minimum value of band gap for the sample doped with a concentration of 2.9 wt % as illustrated in Fig. 8. Above this concentration of 2.9 wt % (3.6 wt %), the band gap energy increases continuously with increasing AgNO$_3$ dopant concentration. The decrease in optical band gap on doping up to a dopant concentration 2.9 wt % may be explained on the basis of the fact that the incorporation of a small amount of dopant forms charge transfer complexes (CTCs) in the host lattice.

![Fig.7: Variation of direct allowed transition using Mott & Davis concept for PVP/Ag composite at 415 nm at different AgNO$_3$ concentration.](image)

![Fig.8: The variation of band gap energy for Ag nanoparticles in PVP at different AgNO$_3$ concentration (%).](image)
The optical band gaps were evaluated also for samples prepared at different gamma irradiation doses ranging from 10 to 50-kGy in a step of 10-kGy at a given constant AgNO$_3$ (Fig. 9). It is clear from the result that the band energy showed a decrease as the dose is increased. Such decrease in the band gap is attributed to further reduction of AgNO$_3$ to Ag nanoparticles, an assumption made also by [19, 20]. The particle becomes smaller as the dose is increased as shown by the TEM imaging. The effect of surface plasmon, which splits to discrete values in the band gap of the composite, leads to a decrease in the general band gap [21].

The weight loss up to this range of temperature is attributed to low molecular weight oligomers, loss of moisture, and residual solvent in this range of temperatures. The second weight loss indicates the degradation of pure PVP above 300 °C, which completely decomposes at 500 °C. The second major weight loss was attributed to structural decomposition of the polymer. The weight loss of Ag/PVP nanoparticles and pure PVP is tabulated in Fig. 11. However, the thermo gravimetric analysis of Ag/PVP nanocomposite showed decomposition profile starting at about 350 °C and continuing until about 480 °C. This shows that the thermal stability of the polymer is improved due to presence of Ag as nano filler. This observation is consistent with the results obtained by [22], where it was shown that the PVA alone starts decomposing at about 280 °C and its composite with less than 1% Ag starts decomposing at higher temperature than the PVA alone which decomposes at about 40 °C or more. In our experiments, though the content of Ag is expected to be more, it appears that the degradation temperature of our composite is higher to what has been reported in the literature.

4. Discussion

However, comparing our results with previous studies may be used as a discussion on the subject. A number of researchers [23-25,31] successfully synthesized Ag nanoparticles. By using electron

\[ \text{Fig. 11: Curve of the TGA thermogram of Ag/PVP nanoparticles and pure PVP showing the weight loss during two stages.} \]
irradiation of silver acetate the particle size of about 40 nm and by using γ-irradiation Ag nanoparticles of 30nm were successfully obtained. Moreover, it was reported in the same experiment that the diameter of Ag nanoparticles tends to reduce in size with the increase of dose. Moreover, a similar result was obtained through the reduction of AgNO₃ by sodium citrate under light irradiation with an average size of 100 nm. Using the chemical method on reduction of AgNO₃ in the presence of sodium polyglutamic acid (PGA) in PVP matrix, similar results of 20 nm Ag nanoparticles were obtained by [26,27]. Earlier Ag nanoparticles have been synthesized in polymethylmethacrilate (PMMA) by 30 kV Ag⁺ ion implantation, which produces Ag nanoparticles with sizes from 2 to 20 nm [28]. Therefore, the diameter of nanoparticles induced by γ-radiation in PVP binder is dependent on the type of binder and radiation dose with respect to the other parameters. This is in conformity with the formation of nanocomposites discussed above.

In the case of the UV-Vis, the blue shift in the plasmon absorption peak reveals that the size of the nanoparticles decreases with increasing gamma dose influence as witnessed from TEM micrographs. Further, the intensity of the absorption bands, which is proportional to the number of silver nanoparticles, goes higher, indicates that more reduction of AgNO₃ to Ag nanoparticale as the dose increases. Similar result was observed by [6] for Ag/PVA prepared by electron irradiation. In addition, similar result was observed for an increase in the amount of AgNO₃ in the composite. The intensity of absorption spectra goes higher but there was a slight shift to higher wavelength as AgNO₃ contents increased in the composites.

These oscillations can give rise to the intense colors for plasmon resonance nanoparticles in PVP. When many Ag are in close proximity, they are able to interact electromagnetically through a dipole-dipole coupling mechanism [29]. Our result is in agreement with the study [30] that investigated the formation of Ag nanoparticles in solution containing 1 mM AgNO₃, 1 mM sodium citrate, and ethanol (0.025 mL) irradiated by γ-rays. Our results also indicate that as the dose was increased, the surface plasmon resonance peak at 415 nm shifted towards lower wavelengths, indicating that smaller diameters of the Ag nanoparticles were also formed at higher radiation doses; the wave length was shifted to higher waves as the AgNO₃ increased. Similar result was observed by [6]. The observation of decreasing band gap for doped samples may be attributed to the fact that their charge transfer complexes increase the electrical conductivity by providing additional charges in the polymer lattice due to the incorporation of Ag nanoparticles with PVP by the influence of gamma irradiation.

However, an additional increase of AgNO₃ dopant concentration leads to segregation of the dopant in the host matrix. These molecular aggregates impede the motion of charge carriers resulting in a decrease in their conductivity and hence increasing the optical band gap energy. Similar results have been reported by [32] on the effect of copper chloride-doping of nylon-6 films. These results point to the fact that a dopant concentration up to 2.9 wt % is the critical concentration that gives optimum values for the optical properties. The incorporation of metal nanoparticles could effectively improve the electrical, optical and dielectric properties of the polymer composites [33,34]. These properties are very much sensitive to small changes in the metal content and in the size and shape of the nanoparticles. It was reported that the nanoparticles themselves could act as conductive junctions between the polymer chains that resulted in an increase of the electrical conductance of the composites [35, 36] leading to a decrease in their optical band gap energy. The morphology and particle size may play an important role in the optical absorption spectra of the Ag/PVP nanoparticles. The above calculated band gap samples have different particle size as shown by the TEM micrographs. The absorption peak due to the surface plasmon resonance of Ag particles can be observed at around 430 nm (Fig. 5) as the volume fraction of Ag increases the surface plasmon resonance peak shift toward longer wavelengths. The shift of the surface plasmon resonance peak position is accompanied by an increase of the absorbance and the width of the peak. The surface plasmon resonance absorption is sensitive to the microstructure of the sample, i.e., size and shape of the dispersed metal particles, concentration of metal phase, and dielectric constant of host medium [37]. In addition, irradiation may change the direction of polarization. This change in the direction of polarization lowers the value of dielectric and as a result, their band gap energy will be reduced. In addition, the size was changed following an increment in dose. The size dependence of the surface plasmon resonance peak position is explained by a size-dependent effective dielectric constant of a metal particle due to the interactions
of conduction electrons [6, 37]. When the particles become much smaller than the mean free path of conduction electrons in the bulk metal, the effective mean free path becomes the dimensions of the particle because electrons are scattered at particle surface. Since the mean size of the Ag particles (~ 8 nm) produced by our method is much smaller than the mean free path of bulk silver (~ 52 nm), such effect must be significant.

However, the morphology could play a strong role in conductivity, which as a result affects both the dielectric loss and dielectric constant. Large particle size leads to electron tunneling, whereas smaller size results in small polaron tunneling and increases with increasing the irradiation doses. As a result, their band gap energy may decrease to lower value. The shift of the band gap position observed in the present study is probably due to the change of the size of the Ag nanoparticles from ~ 6 to ~ 50 nm. The present technique (gamma irradiation) leads an increase of the volume fraction with decreasing size of the Ag nanoparticles as evidence from the TEM images. In addition, irradiation of Ag/PVP samples leads to the formation of Ag nanoparticles and chain scission and cross-linking in the polymer and consequently improved optical properties [9-11]. The inter-particle distance decreases as more Ag is incorporated and as the dose is increased since both factors can decrease the band gap of the composites. This can be explained in terms of morphologies of these composites as revealed by the TEM study. As shown by the TEM micrograph, the majority of nano-size Ag/PVP particles were well dispersed in the PVP when the Ag content range from 0.1 to 0.4 g (0.7 to 2.9 wt %) synthesized at higher gamma dose. Since changes in the volume fraction of metal particles leads to changes in the dielectric constant of the composite due to electromagnetic interaction between neighboring particles, this effect is also thought to be responsible for band gap change [6, 31] in the shift of surface plasmon resonance peak. Therefore, it seems likely that the observed changes in optical absorption spectra for the Ag/PVP nanoparticles can be qualitatively explained by the changes in the effective dielectric constant of the Ag/PVP nanocomposite due to different size and volume fraction of the Ag particles in the PVP, which results with the same effect on their band gap.

The thermal stability is one of the most important and inter related variable, which must be considered carefully when a material is chosen for the synthesis of organic electronic devices. There appears to be an optimal concentration of Ag nanoparticles in PVP maximizing the thermal properties of the materials. Sample with 0.5 g of AgNO₃ was found to be the most suitable and thermal stable. Therefore, the optimized Ag/Polymer nanocomposites materials have the potential to produce organic electronic devices capable of higher thermal stability than pure polymer and leading to many useful applications in organic electronics and nanotechnology.

5. Conclusion

This result indicates that AgNO₃ can effectively dope PVP and enhance the optical and thermal properties. In addition, γ-irradiation is an effective technique for preparing inorganic/organic nanocomposites. The improvement in the optical properties may be attributed to the irradiation with γ-ray that leads to the formation of π-electron clouds, with the polarization aligned in the direction of the molecular chains [32].

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