Physicochemical properties of colloidal Ag/PVA nanoparticles synthesized by gamma irradiation

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Abstract. Silver nanoparticles (Ag NPs) are widely studied because of their superior properties so they are extensively used in various applications. Structural modification with the right synthesis method is the key to obtain superior properties of Ag NPs. In this experiment, gamma irradiation methods have been used to synthesize Ag NPs. The synthesis solution was prepared from a solution of silver metal nitrate salts with a molarity of 10 mM and then mixed in a polyvinyl alcohol (PVA) solution. The irradiation process was carried out in the Cobalt-60 gamma source chamber at a range dose from 0 to 10 kGy with a dose rate of 4.6 kGy/h. This process has caused the solution turns to yellow indicating the formation of Ag/PVA colloidal nanoparticles. The Ag/PVA nanoparticles were characterized using UV-Vis spectrophotometer and Transmission Electron Microscopy. The UV-Vis spectra showed the localized surface plasmon resonance at wavelengths of 420-407 nm. The intensity of the absorption peak increases with increasing gamma dose and reaches a maximum value starting at a dose of 4 kGy. The TEM images showed the shape of Ag NPs is spherical with an average particle size getting bigger with increasing irradiation dose.

1. Introduction

Noble metal nanoparticles have received substantial attention because of their interesting optical and chemical properties which strongly depend on their size and shape [1], [2]. One of the noble metal nanoparticles that have been widely used in various fields of application, such as biomedicine [3], biosensors [4], pharmacy [5], optical sensors [6], and anti-microbial agents [7] is silver nanoparticles (Ag NPs). Ag NPs are widely studied as nanomaterials due to their unique properties such as good electrical conductivity, photoelectrochemical activity, and antimicrobial activity [8]. Ag NPs can be synthesized using various methods such as laser ablation [9], sol-gel [10], photochemical [11], biosynthesis [12] and gamma irradiation [13].

Currently, metal-polymer nanoparticles received a lot of attention because of their optical, electrical and mechanical properties [14]. Here, the metal nanoparticles are dispersed in a polymer medium to improve the performance of nanoparticles such as structural, physical, chemical, optical, electrical and mechanical properties [15], [16]. In many studies, the medium used to synthesize Ag NPs consists of salt precursors, reducing agents, and stabilizers. One of the stabilizers that has been extensively used to synthesize Ag NPs is Polyvinyl Alcohol (PVA) which is one of the water-soluble vinyl polymers.
Among the techniques of synthesizing Ag NPs, the synthesis using gamma irradiation offers some advantages, such as fully reduced metal precursors, highly stable state, and harmless or environmentally friendly [17]. This current research reports the effect of radiation doses on physicochemical properties of Ag/PVA colloidal nanoparticles synthesized using gamma irradiation method and studies the role of PVA in the formation of Ag NPs. PVA was chosen due to its beneficial properties, such as biodegradable, biocompatible, non-toxic, chemically stable, inexpensive and as well as a weak reducing agent[15].

2. Materials and method
2.1. Preparation and synthesis of nanoparticles Ag/PVA
Silver nitrate salt, AgNO₃, was used as a precursor, polyvinyl alcohol (PVA) as a capping agent and double-distilled water as a solvent. AgNO₃ and PVA (MW 60000) were purchased from Sigma-Aldrich. Ag/PVA nanoparticle synthesis was carried out by the gamma irradiation method using Cobalt-60 with an energy range of 1.17-1.33 MeV as gamma sources.

PVA solution was prepared by dissolving 4g of PVA powder into 100 mL of double-distilled water. After that, the PVA solution was heated using a magnetic stirrer at 85°C for 12 h. Around 3 ml of AgNO₃ salt with a molarity of 10 mM was added dropwise to 100 ml of PVA solution. The mixture of the solution was kept under stirring for 3 h at room temperature. The solution of AgNO₃-PVA was irradiated with different doses of 0, 0.5, 1, 2, 4, 6, and 10 kGy in an irradiator Co-60 gamma cell as sources with a dose rate of 4.6 kGy/h at Pusat Aplikasi Isotop dan Iradiasi, Badan Tenaga Nuklir Nasional (PAIR-BATAN), Indonesia.

2.2. Ag/PVA nanoparticles characterization
The Ag/PVA nanoparticles synthesized with various radiation doses were characterized by using a UV visible spectrophotometer (Genesys), Particle Size Analyzer (PSA type Horiba SZ 100z) and Transmission Electron Microscope (TEM TECNAI G2 Spirit Twin). For UV-Vis measurements, 2.0 mL of each sample was taken and the absorbance was observed at a wavelength range of 280-800 nm. For TEM measurements, the same amount of sample was taken and centrifuged twice at 11000 rpm for 60 minutes to remove the excess amount of PVA. After that, the sample was dropped on the TEM grid and then evaporated at room temperature.

3. Results and discussion
It is well known that the interaction of high-energy gamma with materials in an aqueous solution may produce free electrons through photoelectric absorption and Compton scattering processes and also generate the species of strong reductive agents, i.e electron hydrated (e⁻aq) and hydrogen radicals (H⁺) appearing from the process of hydrolysis water [18]. The hydrated electrons and hydrogen radicals can reduce the metal ions (M⁺) to zerovalent state (M⁰) and generate metal atoms from the reduction of metal ion, which eventually coalesce to form aggregates of metal nanoparticles as described by following reactions [19], [20].

\[
\begin{align*}
\gamma \text{-rays} & : \\
H₂O & \rightarrow e⁻_{aq}, H₂O⁺, H⁺, H₂, O H⁺, H₂O₂ \\
M⁺ + e⁻_{aq} & \rightarrow M⁰ \quad (1) \\
M⁺ + H⁺ & \rightarrow M⁰ + H²⁺ \quad (2) \\
nM⁰ & \rightarrow M₂ \rightarrow \ldots \rightarrow Mₙ \rightarrow M_{agg} \quad (3) \\
Mₙ + H₃O⁺ & \rightarrow Mₙ₋₁ + M⁺ + 1/2H₂ + H₂O \quad (4) \\
\end{align*}
\]

In reaction 4, n is a number of aggregation and M_{agg} is the aggregate of the final state. In contrast, at reaction 5, there is the reverse oxidation process which inhibits the reduction process. The reverse oxidation appears from the interaction of H₃O⁺ or OH⁺ radicals with metal atoms (Mₙ) since they
have the capacity to oxidize the ions or the atoms into a higher oxidation state. Thus, to prevent the reverse oxidation process, a scavenger such as isopropanol or polyvinyl alcohol is usually added into the solution [19].

Figure 1 shows the color of Ag/PVA colloid nanoparticles after the gamma irradiation process as a gamma dose function. There was a change in color from colorless for unirradiated samples as control and to yellow for the irradiated samples. As the concentration of silver nitrate in solution increases, the color of the colloidal silver nanoparticles changes from pale yellow to dark yellow [21]. The color change of Ag/PVA colloidal nanoparticles has a similar trend as that obtained by Naghavi et al, which occurs when the irradiation dose increases at a fixed metal salt concentration. The color change of solution indicates the formation of Ag/PVA colloid nanoparticles, which was confirmed by the absorption spectrum from the analyzed of UV–vis spectroscopy.

![Gamma doses (kGy)](image)

**Figure 1.** The color of Ag/PVA colloid nanoparticles after gamma irradiation as a function of gamma dose.

![Absorption spectra of Ag/PVA nanoparticles prepared by gamma irradiation with different doses.](image)

**Figure 2.** Absorption spectra of Ag/PVA nanoparticles prepared by gamma irradiation with different doses.

![Absorbance value of Ag/PVA nanoparticles at 414 nm as a function of gamma dose.](image)

**Figure 3.** Absorption value of Ag/PVA nanoparticles at 414 nm as a function of gamma dose.
Figure 2 shows the typical absorption spectrum of Ag/PVA colloid nanoparticles obtained from a 10 mM AgNO₃ solution at different irradiation doses. In general, the solution of the sample containing silver nitrate salts (10mM AgNO₃), polyvinyl alcohol, and double-distilled water was irradiated by different gamma doses 0, 0.5, 1, 2, 4, 6 and 10 kGy, by the aim to confirm the effect of gamma irradiation doses on the silver nanoparticle formation. The absorption peaks of the Ag/PVA colloid nanoparticles provide SPR bands in the visible light region at wavelengths of 407-420 nm, exhibiting the formation of silver nanoparticles. This absorption peak is associated with the surface plasmon resonance of silver nanoparticles [8]. The SPR of silver nanoparticles has a strong absorbance of electromagnetic waves in the visible region. This shows the optical phenomenon that occurs when light interacts with conductive nanoparticles smaller than the incident wavelength [8]. As the irradiation dose increases, the absorption peak of the Ag/PVA colloid nanoparticles shifts. Meanwhile, at a gamma dose of 0 kGy, there was no absorption peak of Ag/PVA nanoparticles appeared, which means silver nanoparticles had not yet formed, as shown in Figure 2. Furthermore, Figure 2 also shows the characteristic of SPR peak at 420, 417, 416, 407, 414, and 409 nm when Ag/PVA nanoparticles were prepared at different irradiation doses of 0.5, 1, 2, 4, 6, and 10 kGy, respectively. This value corresponds to the experiment of other researchers, where the SPR of silver nanoparticles were found to be in the range of 408-403 nm [22]; 418-431 nm [23]; and 402-396 nm [24].

Figure 3 shows the absorption intensity of Ag/PVA nanoparticles towards the gamma irradiation dose at a wavelength of 414 nm. The wavelength of 414 nm was chosen because it is the midpoint of the absorption area of Ag/PVA nanoparticles at a wavelength of 407-420 nm, that use to show the effect of the different gamma doses used. Based on the graph, the absorption intensity of Ag/PVA nanoparticles increases with increasing irradiation dose. A similar phenomenon occurs in the formation of silver nanoparticles with a green synthesis method, where the effect of reaction temperature provides an important role in the formation of silver nanoparticles. As the reaction temperature increases, the yield of silver nanoparticles increases, this is indicated by the increased absorption intensity of silver nanoparticles. The average diameter of the Ag nanoparticles increased with a higher reaction temperature [8]. Similar results were obtained in this study where particle size increased with increasing doses, confirmed by TEM image analysis.
The full width at half maximum (FWHM) of UV-Vis spectra for Ag/PVA nanoparticles was obtained by the individual fitting using the Gaussian function. Figure 4 shows the FWHM value of Ag/PVA nanoparticle at different irradiation doses. The FWHM value decreases with increasing dose, this shows that the colloidal system of Ag/PVA nanoparticle is increasingly dispersed. At the same time, the shape of the absorption peak provides information about changes in size distribution. As well known, when the solution system is monodisperse (narrow size distribution) the shape of the peak is symmetrical and the value of FWHM is small. Whereas, when the system is polydisperse, the shape of the peak is asymmetrical, which indicates that the peak actually consists of two or more absorption peaks [25]. Figure 3 shows that the shape of the absorption peak changes from asymmetric to symmetric with narrow stabilizers, shown by the decrease in the FWHM value from 67 to 44 nm during the irradiation process, as shown in Figure 4. This means that the colloidal system of Ag/PVA nanoparticle changes from polydisperse to monodisperse. This can be confirmed from the results of TEM images.

![Figure 4](image)

**Figure 4.** TEM images of Ag/PVA nanoparticles with different gamma doses and their distributions (a) 1 kGy; (b) 2 kGy; (c) 6 kGy.
TEM images were used to confirm the morphology and particle size of Ag/PVA nanoparticles. Figure 5 (a) and (b) show the particle size and particle distribution of the Ag/PVA colloid nanoparticles at doses of 1, 2, and 6 kGy, respectively. Based on the analysis of TEM images, Ag/PVA nanoparticles have an almost entirely spherical shape and the distribution of particles is homogeneous. In Figure 5 (a2), (b2), and (c2), the average particle size of Ag/PVA nanoparticles is found to be 10 nm for 1 kGy, 23 nm for 2 kGy, and 25 nm for 6 kGy. TEM image analysis shows that at a small dose of irradiation 1 kGy got a smaller particle size, whereas for larger Ag/PVA nanoparticles size was produced by a higher irradiation dose. Similar results were obtained in experiments conducted by Islam et al. Samples of silver polystyrene polylviny lpyrrolidone nanocomposites at a dose of 40 kGy had an average particle size of 15 nm and at doses of 80 and 120 kGy obtained an average particle size of 35 and 45 nm, respectively [23]. Polyvinyl alcohol plays an important role in the synthesis of Ag nanoparticles because it works as a scavenger and prevents agglomeration of silver nanoparticles. PVA protects Ag nanoparticles from the effects of agglomeration because of their interactions of ion dipoles with OH* radicals [9]. The number of nanoparticles increases with increasing irradiation doses due to an increase in the reduction of silver metal ions. While an increase in the particle size may occur due to faster nucleation of seed particles and subsequent growth to larger Ag NP, as in the report from Yao et al [8]. Yao et al, report that the average diameter of Ag Nanoparticles increased with a higher reaction temperature [8].

Conclusion
The Ag/PVA nanoparticles have been successfully synthesis by the gamma irradiation method in the solution of polyvinyl alcohol. The characteristic absorption peak of Ag/PVA nanoparticles was observed at a wavelength of 420-407 nm. The absorption intensity of Ag/PVA colloid nanoparticles increases with the increase of irradiation dose. The morphology of Ag/PVA nanoparticles has a spherical shape. The particle size increases with an increase in irradiation dose.

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