Silver Nanoparticles on Pullulan derived via Gamma Irradiation Method: A Preliminary Analysis

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Abstract. Radiation induced technique was employed during the synthesis of silver nanoparticles (AgNPs) on pullulan. In this study, the Ag-NPs on pullulan by γ irradiated process is performed to reduce Ag+ ions at the ambient temperature without using excessive reducing agents or producing unwanted by-products of the reductant. Moreover, reducing agent can be uniformly distributed in the solution and AgNPs are produced in highly pure and stable form. The results from ultraviolet-visible spectroscopy (UV-vis) and XRD demonstrated that the silver nanoparticles can be synthesize using pullulan. This can be confirmed by absorption band of UV-vis spectrum at 420 nm as well as the XRD pattern at (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of silver. In addition, the pullulan also acts as a reducing and stabilizing agent. TEM images showed formed AgNPs are spherical in shape with smooth edges. The TEM also revealed that the increasing radiation dose decreases the particle size and increase the rate of reduction. It was found that the mean diameter of silver nanoparticles was about 3.98 -14.87 nm. In addition, the size of the AgNPs is believed can be tuned by controlling the radiation doses. The γ-rays doses also provide the powerful reduction process in a harmless condition by producing a very stable silver nanoparticles.

1. Introduction

Evidence suggest that silver nanoparticles is among the most important metallic in nanotechnology field. This is due to its unique properties which can be incorporated into antimicrobial applications, biosensor materials, composite fibers, cryogenic super- conducting materials, cosmetic products, and electronic components. In addition, the Ag-NPs can be supported on wide range of solid precursor such as silica, metals/metal oxide, carbo, polymer, chitosan and natural fibers [1].

Silver nanoparticles are conventionally produced by the reduction of silver ions from silver salt precursors, with silver nitrate the most frequently used. Reducing agents can be physical (such as UV irradiation, γ-ray irradiation, microwave irradiation, thermal treatment, photochemical process, and sonochemical process), chemical (such as sodium borohydride (NaBH4), dimethyl formamide (DMF), triethanolamine, hydrazine, etc.), or mixed (hydrothermal)[2]. Moreover, biological materials such as plant extracts, bacteria, fungi, and yeast have been used as mediators for the synthesis of silver nanoparticles on extracellular or intracellular level [3].

In recent years, there has been an increasing interest in the fabrication of metal nanoparticles using various saccharides such as glucose, sucrose, starch, chitosan, and marine polysaccharide [4]. The said approach is regarded as a green method which is safe, biocompatible, nontoxic and environmentally friendly process for the synthesis of metal nanoparticles [3].

The past decade has seen the rapid development of pullulan used in synthesis the silver nanoparticles mainly in conventional chemical reduction techniques. Pullulan is a linear glucosic polysaccharide produced by the polymorphic fungus *Aureobasidium pullulans*, which has long been applied for various applications from food additives to environmental remediation agents. To date, surprisingly synthesizing the Ag-NP on pullulan by γ-irradiation method has not been closely studied. The previous study mainly focusing the usage of pullulan and other starch derivative as a capping agent and stabilizer in producing the Ag-NP. Several studies make a research in utilizing the pullulan to produce metallic nanoparticles and limited their process by applying the conventional chemical reduction process [5–9].

Here, in this study reports a simple γ-irradiation method in producing the AgNPs on pullulan. The radiation method offers many advantages for the preparation of metal nanoparticles. Hydrated electron, resulted from the gamma radiolysis of the aqueous solutions, can reduce metal ions to zero-valent metal particles, avoiding the use of additional reducing agents and the consequent side reactions. This novel gamma irradiation technique was chosen due to its clean and inert process. In addition, this method also provides the faster reaction times, higher yields and improve material properties [9].

2. Materials and method

All material and reagents used in this work were analytical grade and used as received without further purification. Silver Nitrate ($AgNO_3$-99.85%) was used as the silver precursor, which was obtained from Acros Organic (USA). The Pullulan powder (R&M Chemicals, UK) was applied as a solid support for Ag-NPs. All these aqueous solutions were used with double distilled water.

2.1. Synthesis of AgNPs/PL

The initial stage involved the formulation of silver nanoparticles (AgNPs) on Pullulan (PL) by γ-irradiation. The synthesis of AgNPs/PL was start by dispersing 3.0 g of Pullulan in 100 mL double distilled water and consistently stirred for 1 hour at 90°C until clear solution is obtained. The solution of PL is left to cool at the ambient temperature and thereafter 100 mL of aqueous solution of $AgNO_3$ (0.1 mol/L) was added and the mixture was further stirred for 1 hour. The mixture was then divided into six equal parts (20 ml) sample bottle, purged by N_2 for 30 minutes and sealed. Finally, the suspension which contained $AgNO_3$/PL (A0), was irradiated under γ-irradiation with absorbed doses of 5, 10, 15, 20, 25, and 50 kGy (A1-A6). γ-irradiation process was carried out in a ^{60}Co Gammacell irradiator at room temperature (the dose rate is at 35.7 kGy/min) which was provided by Malaysian Nuclear Agency, Bangi.

2.2. Characterization Methods and Instruments

The formation of Ag-NPs was confirmed using UV-Vis Spectroscopy analysis. The produced Ag-NPs were scanned from the 300-1000 nm with UV-Vis Spectrophotometer (UV-2600 Shimadzu, Japan) at medium rate scan. The spectra of the sample were measured using ad designed holder for sample of 2 cm x 2 cm dimension. It is known that UV-vis analysis can be used to determine the peak of the metal atoms. The peak detection is due to the coloured metal ions in response with the absorption of visible light. In addition, the electrons within the metal atoms excited one electronic state to another leading the sharp peak presence at a specific range.

The crystallinity of the nanomaterials was determined by XRD analysis. In this analysis the XRD pattern was started to scan from 10° to 80° at 2Θ angle. The identity of the silver nanoparticles can be confirmed by comparing the XRD pattern with the library. The XRD samples were dropped until certain thickness in the thin film by repeatedly dropping and drying at 60°C. The structure of the produced Ag-NPs was examined using XRD-Empyrean (PANalytical, United Kingdom).

The TEM sample was prepared by dropping the Ag-NPs on the surface of carbon coater copper grid. The morphology and size of the nanoparticles were determined by this technique. The dried sample was scanned using JEM-2100F transmission electron microscope (JEOL, Japan).

3. Results and discussion

Silver nanoparticles on pullulan (Ag-NPs/PL) were produced by the reduction of $AgNO_3$ into Ag^+ assisted with the fragmentation of large Ag-NPs during γ-irradiation. The prepared sample of silver nanoparticles on pullulan were shown in Figures 1. The colour intensity of the prepared Ag-NPs/PL samples were gradually increased. The A0 AgNP/PL suspensions without γ ray shown the light brown solution. As the γ-rays increased the suspension marks a dark brown solution (A3-A6). Pullulan solution is transparent without colour. The solution of AgNPs/PL are changing from light brown to dark brown solution after gamma irradiation process.

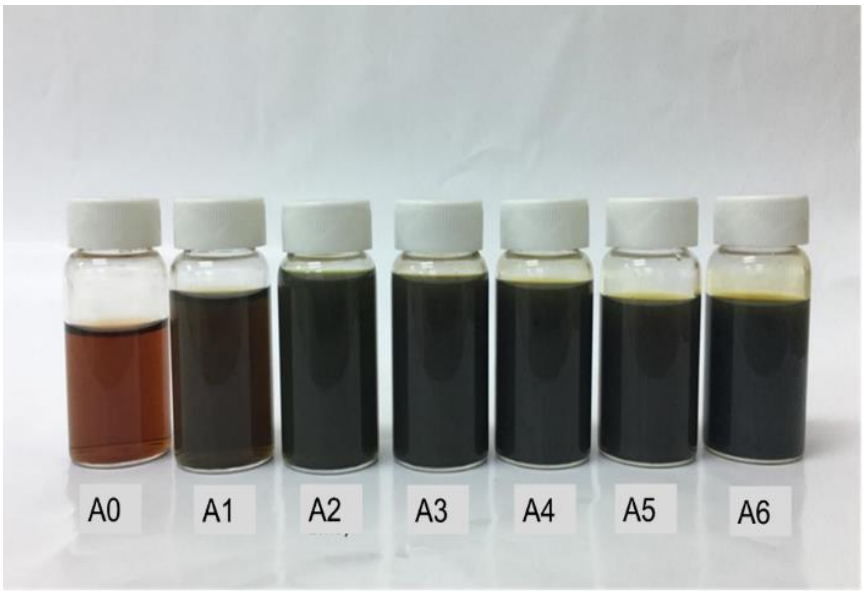


Figure 1. Photograph of Ag-NPs/PL at different γ-irradiation doses; 0, 5, 10, 15, 20, 25, 50 kGy (A0-A6)

3.1 UV-vis analysis

In this study the formation of Ag-NPs with different gamma radiation dose were monitored using UV-Vis spectroscopy. UV-Vis analysis is a top screening analysis in confirming the formation and strength of silver nanoparticles. Figure 2 shows the UV-Vis absorption spectra of the Ag-NPs/PL at different gamma rays dose. This result revealed that the Ag-NPs/PL prepared at 50 kGy, 25 kGy, 20 kGy, 15 kGy, 10 kGy and 5 kGy produced absorption spectra with sharp peaks (surface plasmon resonance, SPR) at 420 nm. On the other hand, the Ag-NPs/PL prepared without gamma radiation, the SPR peaks was not appeared at 420 nm indicating of no Ag-NPs produced. As the irradiation dose increased (from 10 to 50 kGy) the SPR peak position is shifted from 420 nm to 410 nm indicating the formation of smaller particles [10]. The most prominent sharp SPR peak can be obviously seen for Ag-NPs/PL prepared at 50 kGy, 25 kGy and 20 kGy. The peak intensities were higher at higher gamma dose justifying the highest yield of Ag-NPs with a highly uniform particle size [11]. The highest gamma doses was set at 50 kGy to shows the different sample performance between 25 kGy and 50 kGy.

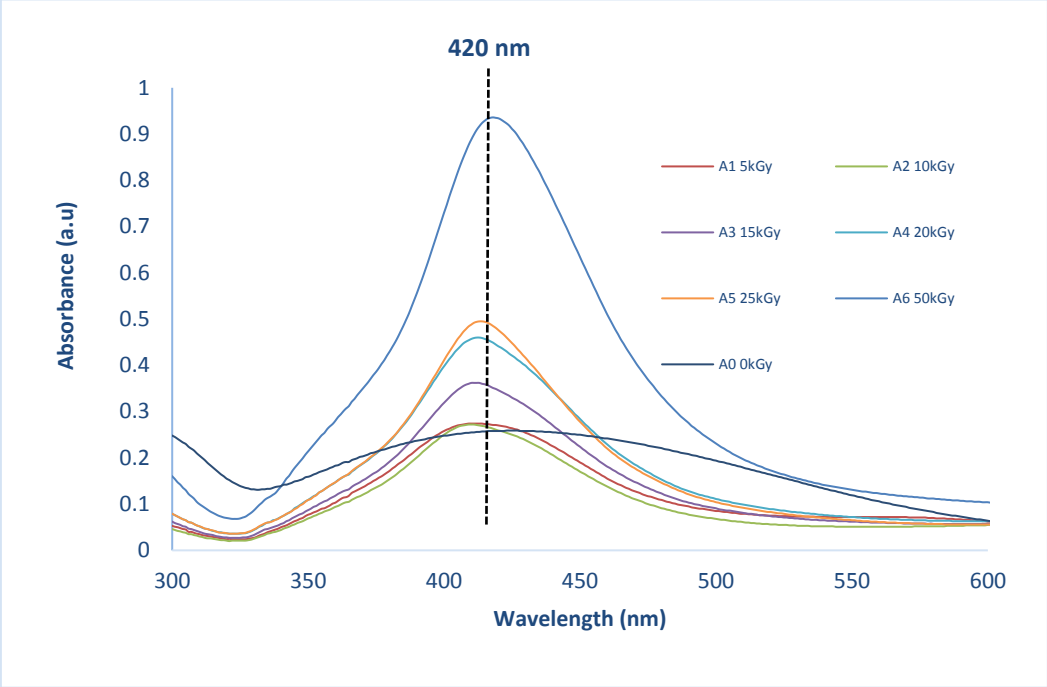


Figure 2. UV-Vis spectrum of the Ag-NPs/PL prepared at 0, 5, 10, 15, 20, 25, and 50 kGy gamma doses.

3.2 XRD analysis

X-ray diffraction (XRD) analysis is one of the most important conformational techniques in the current study. The crystalline region and purity of the AgNPs play an essential role in determining the quality of AgNPs properties. Figure 3 shows the XRD patterns of AgNPs/PL. The purity and crystallinity of synthesized AgNP/PL is confirmed. This can be proved by four (4) diffraction peaks with the 2Θ of 38.20, 44.0, 64.20, and 77.40 corresponding to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of the face-centered cubic (FCC)[24]. The notable four diffraction peaks are in good agreement with the theoretical standard figures (JCPDS file no. 01-087-0718). The sample of formulation A1-A5, indicated the prominent silver in their crystalline phase without any significant traces of other phases. In addition, the occurrence of nanosized particle of AgNP/PL helps in shaping the wide and sharp XRD patterns peaks [12].

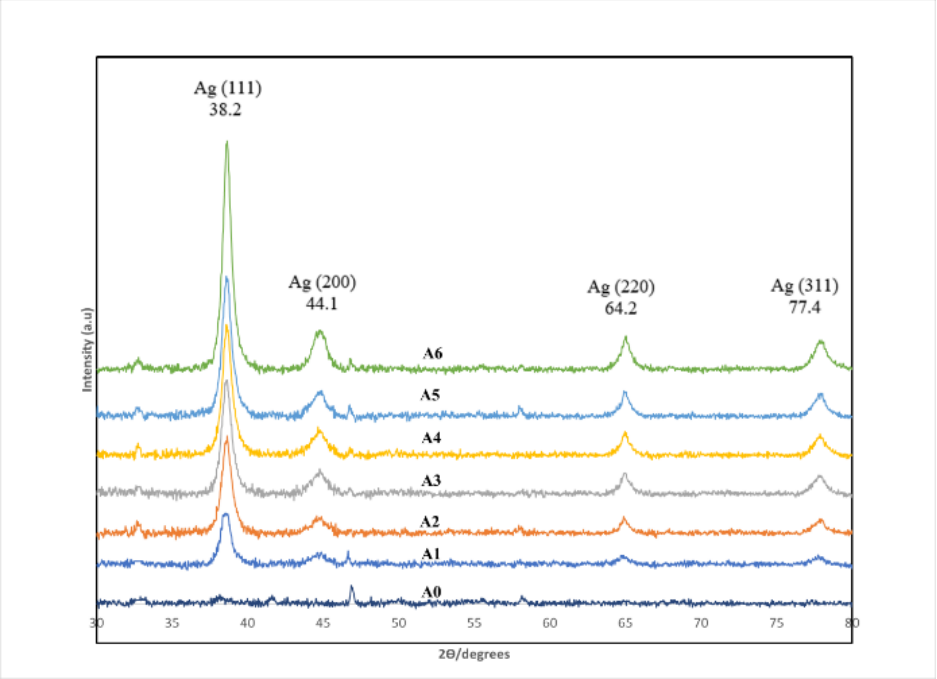
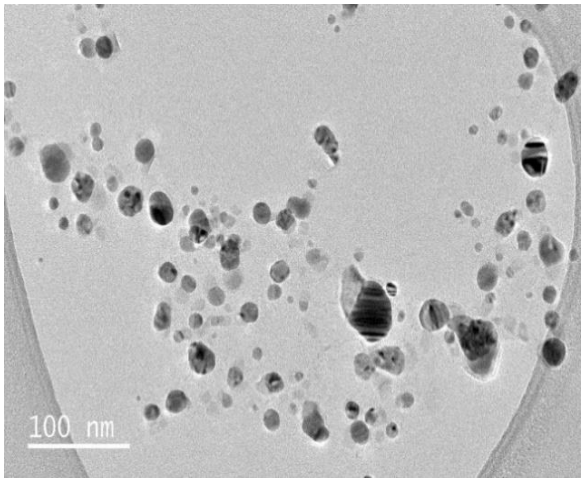
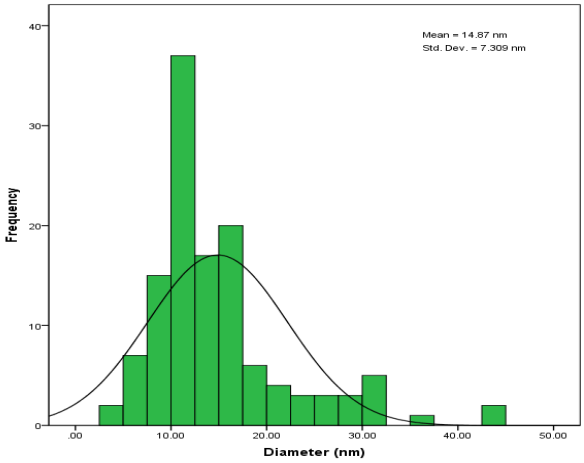


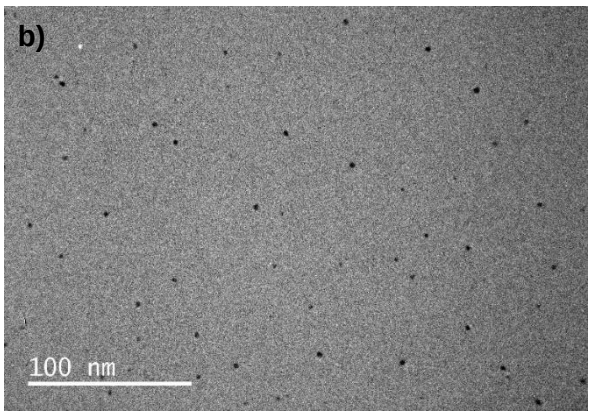
Figure 3. XRD patterns of AgNP/PL at different γ-irradiation doses; 0, 5, 10, 15, 20, 25, and 50 kGy (A0-A6)

3.3 TEM analysis

To evaluate the morphology and particle size distribution of the obtained AgNPs, the Transmission Electron Microscopy (TEM) imaging was conducted. The TEM micrograph clearly revealed that the silver nanoparticles are well dispersed in the pullulan matrix as shown in Figure 4 a), b) [9]. In addition, the AgNPs were also segregates evenly with almost no aggregates are seen. The spherical and oval shape were also observed in the TEM images[2]. It is definitive that the γ-ray reduced the particle size distribution during the irradiation process. The particles size distribution (mean diameter and standard deviation) was noted at 3.98±1.356 nm at 50 kGy dose and 14.87±7.309 at 25 kGy indicating of the evenly AgNPs segregating process [2]. The particles size distribution (mean diameter and standard deviation) was drastically decreased to 3.98±1.356 nm at 50 kGy dose indicating of the evenly AgNPs segregating process [2] The combination of nanostructures at different sizes are leading to the broadness of the size distribution peaks in Figure 4b), proving that the particles at high γ-doses were highly uniform and homogenous. In addition, at 50 kGy γ-ray doses shows the finer size of silver nanoparticles indicative of hydrated radicals ($\bar{e}$ aq) are fully produced thus, promoting the reduction of silver ions to silver atoms [13]. It is also found that the pullulan not only function as stabilizer during the synthesis of silver nanoparticles but also as capping agent by providing the template in radiolysis process.







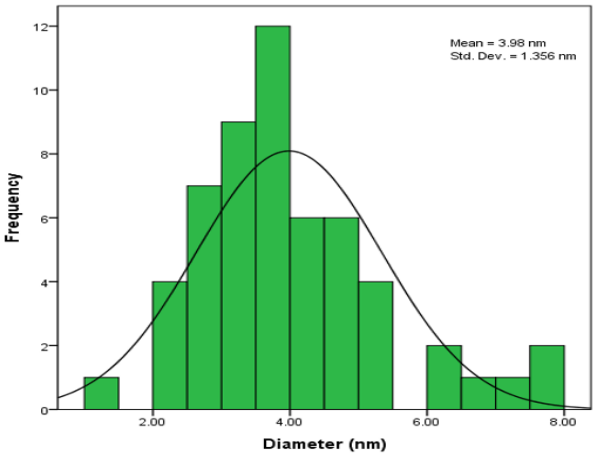


Figure 4. TEM images and their corresponding particle size distribution of AgNP/PL at a) 25 and b) 50 kGy

4. Conclusion

In conclusion, the silver nanoparticles on pullulan was successfully synthesized. The stable AgNPs/PL were prepared without using any chemical reducing agent. This green approach was also believed as a rapid, single step and effective method in producing AgNPs/PL. The UV-visible spectroscopy

confirmed the formation of silver nanoparticles by the detection of plasmonic band at 420 nm. The XRD pattern showed that the crystalline structure of the AgNPs for all sample were fcc. TEM imaging ascertained that the AgNP were observed as spherical and oval shape and very well dispersed in pullulan matrix. It is also noted that the γ-irradiation techniques provide Ag-NPs in completely reduced, extremely pure, and very stable states. In addition, there is no undesirable impurities like silver oxide are introduced.

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