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Preparation of colloidal silver nanoparticles in poly(*N*-vinylpyrrolidone) by γ-irradiation

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Colloidal silver nanoparticles were prepared by γ-irradiating Ag^+ in aqueous solution in the presence of 2% polyvinyl pyrrolidone (PVP) as stabilising agent and ethyl alcohol as free radical ($OH^\bullet$) scavenger. The saturated conversion dose of Ag^+ into Ag was determined by UV–Vis spectroscopy and the silver nanoparticles size was characterised by transmission electron microscopy. The influence of Ag^+ concentration (1–50 mM) on the saturated conversion dose and average diameter of silver nanoparticles was investigated. Results showed that the saturated conversion dose was from 8 to 48 kGy and the silver particles size was in the range of 6–21 nm for Ag^+ concentration from 1 to 50 mM. The effect of PVP molecular weight on silver particles size was studied as well.

Keywords: colloidal silver nanoparticles; polyvinyl pyrrolidone (PVP); γ- irradiation

1. Introduction

The synthesis of silver nanoparticles has attracted considerable interest due to their novel physicochemical properties and their potential applications in many fields such as medicine [1] (http://lifesilver.com/safety.html), textiles [2,3], sensors and detectors [4], catalysis [5], nanocomposites [6,7] as well as agriculture [8]. The antibacterial activity of silver-containing materials such as polyurethane foam can be used for water treatment [9].

Many methods (e.g. chemical [10–13], electrochemical [14] and photochemical reduction [15], ultrasound [16], microwave [17] gamma and electron irradiation [18–24]) for the synthesis of silver nanoparticles with different stabilisers have been developed.

The size of nanoparticles obtained varies from system to system not only because of the method but also because of the other parameters such as stabiliser and

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metal ion concentration. The possibility of a precise control of particle size and mass production remains the most attractive goal for the synthesis of silver nanoparticles.

A method using ionising radiation (gamma and electron) provides several advantages compared to other methods [13–17], such as: (1) the process is carried out at room temperature; (2) reducing agents fairly uniformly occur in the irradiated solution; (3) the reaction rate can be reliably controlled by varying irradiation time; (4) colloidal silver nanoparticles can be purely prepared without contamination of excessive reductant and silver ion residue; (5) the size of the particles is easily controlled by varying silver ion concentration; (6) mass production can be carried out at a comparatively reasonable cost.

The mechanism of the γ-ray irradiated method was described in the previous papers [18,21]. Briefly, Ag^+ ions were reduced by hydrated electron (e^-_{aq}) and hydrogen atom ($H^\bullet$) which were generated by γ-radiolysis of aqueous solution as described in Equation (1).

$$H_2O \xrightarrow{\gamma-\text{radiation}} e^-_{aq},\ H^\bullet,\ OH^\bullet,\ H_2O_2,\ H_2,\ H_3O^+, \ldots s \tag{1}$$

The solvated electrons with $E^0(H_2O/e^-_{aq}) = -2.87\,V_{NHE}$ and $H^\bullet$ atoms with $E^0(H^+/H^\bullet) = -2.3\ V_{NHE}$ are powerful reducing agents so that they easily reduce Ag^+ ions to the zero-valent state Ag^0 with $E^0(Ag^+/Ag^0) = -1.8\ V_{NHE}$ as shown by (2)–(4). The reaction process can be written as follows:

$$Ag^+ + e^-_{aq} \rightarrow Ag^0 \tag{2}$$

$$Ag^+ + H^\bullet \rightarrow Ag^0 + H^+ \tag{3}$$

$$Ag^0 + Ag^+ \rightarrow Ag_2^+ + \cdots \rightarrow \quad Ag_{n+1}^+. \tag{4}$$

The hydroxyl radical ($OH^\bullet$) reacts with alcohol (e.g. methanol, ethanol, isopropanol...) yielding hydroxylakyl radical which is able to reduce Ag^+ ions absorbed on clusters to zerovalent silver.

$$RCH_2OH\ (R_2CHOH) + OH^\bullet \rightarrow R^\bullet CHOH\ \left(R_2^\bullet COH\right) + H_2O \tag{5}$$

$$R^\bullet CHOH\ \left(R_2^\bullet COH\right) + Ag_{n+1}^+ \rightarrow Ag_{n+1}^0 + RCHO\ (R_2CO) + H^+ \tag{6}$$

Alcohol is called upon as a free radical ($OH^\bullet$) scavenger. The $R^\bullet CHOH$ radical with $E^0(RCH_2OH/\ R^\bullet CHOH) \approx -1.8\ V_{NHE}$ is not able to reduce free Ag^+ ions in solution while they can reduce Ag^+ ions in cluster Ag_{n+1}^+ due to $E^0(Ag^+/Ag_n^0) = 0.78\ V_{NHE}$ [25].

Several studies to prepare silver nanoparticles by γ-irradiation method using polyvinyl pyrrolidone (PVP) as stabiliser were reported [19–21]. Shin et al. [19] studied the mechanism of growth of colloidal silver nanoparticles stabilised by PVP in γ-irradiated silver nitrate ($AgNO_3$) solution. Li et al. [21] prepared silver nanoparticles by γ-irradiation and chemical reduction with citrate in order to compare both methods. According to their results, when the same starting $AgNO_3$ solution 1.0×10^{-3} M was used for the both methods, the particles size of silver (13 ± 2 nm) for γ-irradiation was smaller than that for chemical reduction (23 ± 6 nm). However, in the above mentioned papers the influence of Ag^+ concentration on saturated conversion dose and particles sizes was not systematically studied.

In this work, γ-irradiation of Ag^+ ions with various concentration from 1 to 50 mM in aqueous PVP was studied. The effect of PVP molecular weight on silver particles size was also investigated.

2. Experimental

2.1. *Chemicals*

Silver nitrate, ethanol (C_2H_5OH) and PVP (PVP K90, $M_w = 1.1 \times 10^6$ and PVP K30, $M_w = 5.0 \times 10^4$), analytical grade products from Merck, Germany were used as received. Pure water for chromatography was used throughout in this study.

2.2. *Preparation of colloidal silver nanoparticles by γ-ray irradiation*

The solutions contained 2% PVP, 0.5 M ethanol and Ag^+ with different concentration from 1 to 50 mM in glass tubes, which were deaerated by bubbling with nitrogen. The γ-ray irradiation was carried out on a Co-60 source with dose rate of 1.63 kGy h^{-1}, at VINAGAMMA Center, Ho Chi Minh City.

2.3. *Characterisation*

Absorption spectra of silver nanoparticles solution which was diluted by water to 0.1 mM calculated as Ag^+ concentration were taken on an UV–Vis spectrophotometer model UV-2401PC, Shimadzu, Japan. The size of the silver nanoparticles was measured using a transmission electron microscope (TEM) model JEM 1010, JEOL, Japan, operated at an accelerating voltage of 80 kV.

3. Results

The radiation dose required for complete reduction of Ag^+ into metal silver is defined as the saturated conversion dose and it is important for synthesising the product of colloidal silver nanoparticles practically free from Ag^+ precursor.

The values of optical density (OD) of the irradiated solution at different doses are shown in Figure 1. The OD of surface plasmon resonance of silver cluster increased up to a maximum at the dose that was specified as the saturated conversion dose and thereafter it remained constant or slightly decreased in some cases. Figure 2 presents the UV–Vis spectra of colloidal silver nanoparticle at the saturated conversion dose. It can be observed from Figure 2 that the lower the initial silver ion concentration the higher the value of OD that was attained. The results in Figure 3 show that the saturated conversion dose is in the range of 8–48 kGy for Ag^+ concentration from 1 to 50 mM. They indicate that the higher the Ag^+ concentration, the higher the dose that should be provided. Results of particles size (d, nm) calculated from TEM images and the maximum wavelength (λ_{max}, nm) at the saturated conversion dose are presented in Figure 3. It was also evident from the red shift of surface plasmon resonance bands from 405.5 nm (1 mM) to 421.0 nm (50 mM). A similar trend was also observed by Li et al. [21] and Du et al. [24] in their studies on the

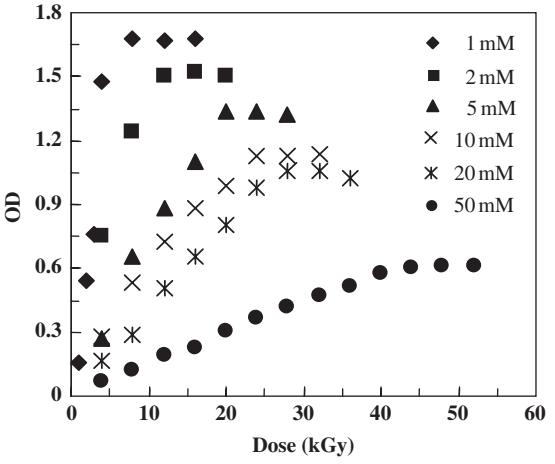

Figure 1. The relationship of OD of irradiated Ag^+ solution with dose.

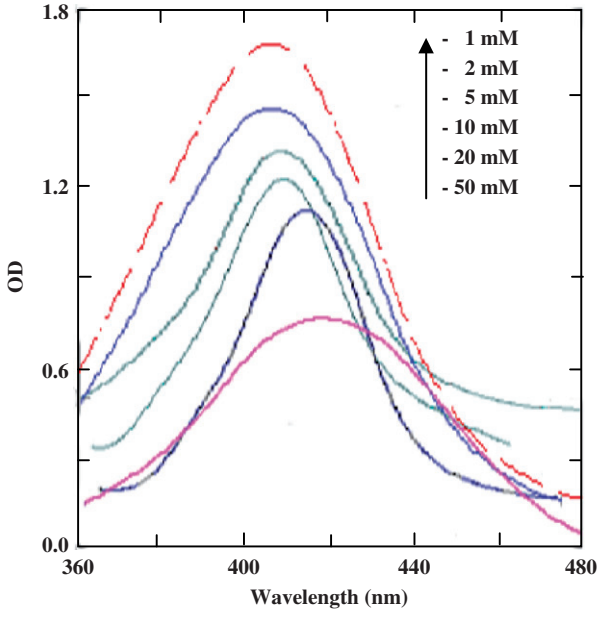

Figure 2. UV–Vis spectra of colloidal silver nanoparticles at the saturated conversion dose.

radiation-induced synthesis of silver nanoparticles stabilised by PVP and PVA. The particles size was obtained to be in the range of 6–21 nm for Ag^+ concentration from 1 to 50 mM.

A typical photograph of silver nanoparticles and the particles size distribution as a histogram are shown in Figure 4. The particles were quasi-spherical in shape and the size distribution was of the Gaussian type. The average diameter of silver nanoparticles

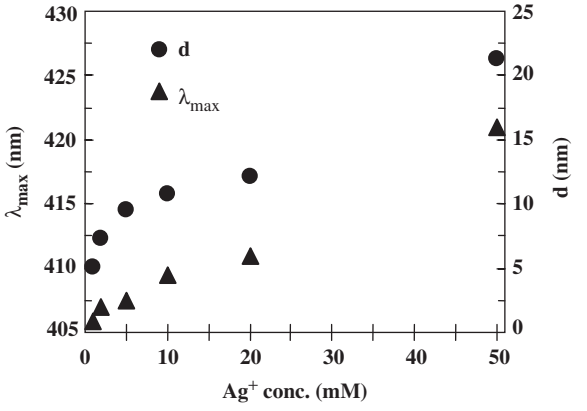

Figure 3. The relationship of λ_{max} and d of silver nanoparticles to Ag^+ concentration.

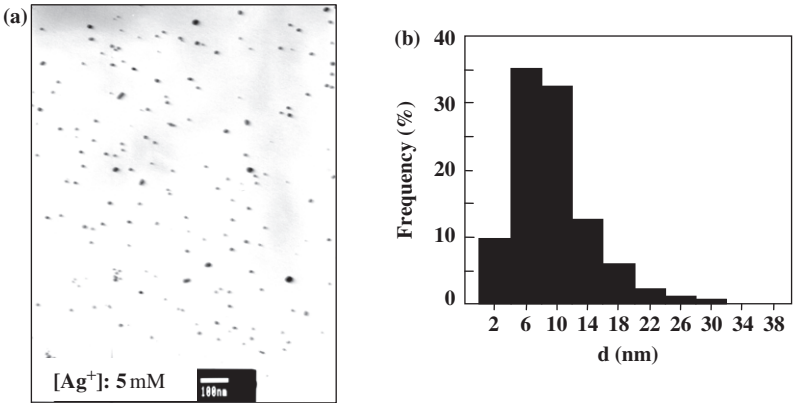

Figure 4. The TEM image (a) and particles size distribution (b) of silver nanoparticles for sample of 5 mM Ag^+.

calculated by manual counting was about 9.52 ± 0.80 nm for Ag^+ concentration of 5 mM. In comparison with the particle size of 17 ± 3 nm prepared by Li et al. [21] using the same Ag^+ concentration (20 mM), the particles size of 12.17 ± 1.79 nm (Table 1) obtained in our work was smaller. The reason may be explained by the different M_w and concentration of PVP.

The average size of the silver nanoparticles was reduced with the increase of molecular weight of PVP (Table 1). A similar result was also observed by Temgire and Joshi using PVA as stabiliser [26]. Our result on the effect of PVP molecular weight on the particles size was controversial in the light of the results reported by Shin et al. [19]. The reason was still unknown. Shin and co-workers proposed a three-step mechanism for the growth of the silver nanoparticles as following: (1) the silver ions interact with PVP; (2) the silver ions reduced to silver atoms which aggregate to silver clusters or silver primary nanoparticles by exposing to γ-irradiation; (3) these clusters agglomerate with others nearby to form

Table 1. The effect of PVP with different molecular weight on λ_{max}, OD and d.

PVP (M_w)	Conc. Ag^+ (mM)	λ_{max} (nm)	OD	d (nm)
5×10^4	20	417	0.9000	21.69 ± 1.86
110×10^4	20	411	1.0574	12.17 ± 1.79

final nanoparticles. In addition, they explained that the reason larger particles size resulted using PVP with high molecular weight was due to interaction with more silver ions per polymer molecule. During irradiation, there were more silver ions in close proximity within a PVP and this resulted in final silver nanoparticles of larger size [19]. According to our results, such an explanation was inadequate due to the fact that PVP with higher molecular weight can effectively prevent agglomeration of clusters or primary nanoparticles to form larger size. Yin et al. [14] studied electrochemical synthesis of silver nanoparticles under protection of PVP with different molecular weight, particularly PVP K17, PVP K30 and PVP K90. They also reported that silver nanoparticles stabilised by PVP with higher molecular weight (PVP K30, PVP K90) exhibited a well-defined absorbance peak, whereas those obtained by stabilisation with lower molecular weight (PVP K17) did not show any peak under identical condition [14]. This meant that silver colloids obtained under protection of PVP K17 were of large silver particles. They also proposed that PVP with a short polyvinyl chain (low molecular weight) was unfavourable for the electrochemical synthesis of silver nanoparticles. Further work should be carried out to clarify this phenomenon. However, it was strongly believed that the tendency would be as same as our results.

4. Conclusion

Colloidal silver nanoparticles stabilised with PVP were prepared by γ-irradiation method. The wavelength at the maximum absorption shifted towards a longer one with the increase of the initial concentration of Ag^+ ions. It indicated that larger size particles were formed in the irradiated solution of higher Ag^+ concentration, particularly from about 6 nm (1 mM) to 21 nm (50 mM).

A smaller size of silver nanoparticles was resulted by using PVP with high molecular weight as stabiliser. The unique features of the γ-irradiation method are convenient especially for the production of colloidal silver nanoparticles on a large scale.

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