A Facile Route in Controlling the Optical Absorbance of Polyvinylpyrrolidone-Capped Silver Nanoparticles Via Chemical Reduction Technique

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Abstract. This work presents the synthesis of silver nanoparticles (AgNPs) capped with polyvinylpyrrolidone (PVP) via a simple chemical reduction approach. A route in controlling the optical absorbance of the AgNPs by varying the concentration of silver precursors, as reflected by the shifts and broadening of the UV-vis spectra of the AgNPs is also highlighted. Dynamic Light Scattering results revealed the narrow and small hydrodynamic size for AgNPs synthesized at low precursor concentration, while multiple hydrodynamic size peaks were observed for AgNPs produced at high precursor concentration. Likewise, Fourier transform-infrared spectroscopy confirmed the successful capping of PVP on the AgNPs through the O and N atoms as potential binding sites. Transmission electron micrographs revealed the formation of spherical PVP-capped AgNPs, having no apparent aggregation observed. A closer inspection of the micrograph showed the subsequent formation of rod-like growth template of the AgNPs, that might lead to the formation of non-spherical silver nanostructures.

Keywords: silver nanoparticles, polyvinylpyrrolidone; optical absorbance; transmission electron microscopy

1. Introduction
The unique properties of silver nanoparticles (AgNPs) have been extensively studied due to their promising applications in a wide variety of technology. In fact, silver nanoparticles are now being incorporated in various products, including conductive pastes and inks, photovoltaic cells and devices, antimicrobial coatings and dressings, and molecular diagnostic devices and colorimetric sensors [1].
Unlike its bulk counterpart that has a lustrous grayish color, AgNPs may appear in diverse colors depending on the nanoparticles' size and shape [2]. For instance, AgNPs with a spherical particle size of around 5 nm has a pale yellow color while AgNPs at around 40 nm and 100 nm have a greenish and grayish color, respectively [3]. This interesting property of AgNPs is credited to the strong collective oscillation of the electron cloud on the surface of the nanoparticles in the presence of light, which is commonly termed as surface plasmon resonance (SPR) [4]. Because of their tunable SPR, AgNPs have become versatile materials for emerging researches that aim to explore the diverse and unique applications of AgNPs, particularly in the field of sensors, photovoltaics, and photonics [5].

In exploiting AgNPs as an outstanding functional material, stability and tunability are two of the most important criteria that should be considered. It has been known that AgNPs are very sensitive to the changes of its environment [6]. In fact, minimal modification on its surface chemistry via chemical or physical interactions might induce significant changes in its stability, leading to aggregation and deterioration in terms of physical and optical properties [7]. To enhance the stability of AgNPs, stabilizing agents are being introduced in the synthesis process that may also act as a capping agents to provide specific functionalities [6,7]. Typical capping agents consist of polar head groups that link to the nanoparticles’ surface and nonpolar hydrocarbon tails that interact with the surrounding media. Polymers, dendrimers, and biological extracts are commonly utilized as capping agents depending on the nature and application of the nanoparticles [8].

Poly(vinylpyrrolidone) or PVP is a very common water-soluble polymer that is used as a binder in pharmaceutical pills. It is also found in disinfectant solutions, liquid soaps, scrubs, ointments, and other medical and commercial products [9]. Together with its availability and affordability, PVP is considered as a promising capping agent for nanoparticles due to its biocompatibility. In fact, a number of work reported the successful synthesis of AgNPs incorporating PVP as a capping and stabilizing agent using various synthesis techniques. For instance, Kittler et al. reported the synthesis of PVP-coated AgNPs via the polyol process and its bioactivity towards human stem cells [10]. Also, Xiliang, et al. highlighted the large-scale synthesis of AgNPs with PVP for low-temperature sintering bonding application [11]. PVP was also incorporated on AgNPs synthesized from bacterial supernatant, as demonstrated by Bhatia and colleagues [12]. Among these successful routes in synthesizing AgNPs with PVP, the chemical reduction has remained the easiest and fastest way to produce stable nanostructures [13-15]. Although the incorporation of PVP to AgNPs has been previously studied and elaborated, the influence of various synthesis parameters on the properties of PVP-capped AgNPs is still a wide area to investigate. Moreover, tuning the properties of the PVP-functionalized AgNPs by manipulating the key synthesis parameters is still an open area for further exploration. Specifically, the effect of silver precursor concentration in controlling the optical absorbance of PVP-capped functionalized AgNPs has never been fully elucidated. Hence, this work demonstrates a simple route to manipulate the optical absorbance of PVP-capped AgNPs by varying the volume of silver precursor used in the chemical reduction process.

2. Experimental details

2.1 Chemicals and Materials
Silver nitrate (Sigma Aldrich, 99.8%) was used as the silver precursor. Both sodium borohydride (Sigma Aldrich, 99.9%) and sodium citrate (Sigma Aldrich, 99.8%) were used as reducing agents. PVP was also used as a stabilizer and capping agents. Double deionized water was used in preparing all solutions needed in this study.

2.2 Preparation of PVP-capped AgNPs
Silver nanoparticles (AgNPs) were prepared using a simple chemical co-reduction of silver nitrate in sodium borohydride and sodium citrate solution as demonstrated by previous works [13-15] but with some modifications. In brief, a known volume of 0.02 M sodium borohydride and 0.02 M sodium citrate were mixed and stirred for 30 minutes at room temperature. A known volume of silver nitrate (0.001-0.02 M) was added dropwise to the sodium borohydride-sodium citrate mixture. After the addition of
silver nitrate, the color of the solution changed from clear to yellow, indicating the formation of AgNPs. Drops of 1% PVP were then added to stabilize the AgNP solution. To tune the optical absorbance of the AgNPs, an additional volume of the silver precursor was simply supplied to the mixture until the desired color change was observed.

2.3 Characterization of AgNPs
UV-visible (UV-Vis) spectroscopy was employed to examine the optical property of synthesized AgNPs using a Perkin multimode microplate reader. Fourier transform-infrared (FT-IR) spectroscopy was used to identify the functional groups present in the samples. Furthermore, a dynamic light scattering (DLS) technique was used to determine the hydrodynamic size distribution. Lastly, transmission electron microscopy (TEM) was used to investigate the morphology and size of the PVP-capped AgNPs.

3. Results and discussion
The optical absorbance spectra of the PVP-capped AgNPs in response to the variation in the precursor concentration is presented in figure 1. The change in the appearance of the mixture from clear to yellow indicated the successful formation of AgNPs. It was observed that with lesser concentration of AgNO₃, a pale yellow AgNP solution was obtained, that produced a narrow and symmetric optical absorbance spectrum with a peak at 402 nm. This spectral behavior may be attributed to the SPR of small and monodisperse AgNPs [15]. Increasing the concentration of silver precursor to 0.003 M resulted in the production of intense yellow AgNP solution projecting a symmetric spectrum with a red-shifted peak at around 408 nm. It has a wider spectrum compared to the previous that might suggest the subsequent growth of AgNPs into larger sizes [16-18]. Increasing the concentration of silver precursors further resulted in the production of deep yellow to orange AgNP solution, which projected a gradual widening and asymmetry of the absorbance spectrum, suggesting the continuous growth of the AgNPs. Further increase of the precursor up to 0.02 M resulted in red-orange AgNPs solution with an asymmetric UV-Vis spectrum with two absorbance peaks located at 405 and 555 nm, respectively. This broad and asymmetric UV-Vis profile may be associated with the overlapping SPR bands of a polydisperse population of PVP-capped AgNPs [19]. However, several results attribute the broadening of the peak at around nm 600 to the gradual formation of non-spherical and asymmetric aggregates of AgNP crystals such as nanorod structures [20-22]. It is also worthy to mention that in the absence of PVP, AgNPs synthesized using 0.02 M of precursor concentration exhibited an abrupt aggregation as manifested by the low intensity and wide absorbance profile in figure 1(b).

![Figure 1](image-url)

**Figure 1.** (a) Normalized UV-Vis spectra of the PVP-capped AgNPs synthesized using a varied concentration of silver precursor and (b) UV-vis spectra of AgNPs synthesized with 0.02 M precursor concentration with and without PVP as a capping agent.
DLS technique was employed to investigate the change in the hydrodynamic size of the PVP-capped AgNPs, as presented in figure 2. For brevity, only the DLS profile of the PVP-capped AgNPs synthesized using 0.001 M, and 0.02 M precursor was shown. The AgNP derived from low precursor concentration projected a mean hydrodynamic size of 21.10 nm with a polydispersity index (PI) of 0.264. According to literature, PI values that are less than 0.3 suggest a good dispersity of nanoparticles in an aqueous medium [23]. On the other hand, the DLS profile of AgNP produced from high precursor concentration exhibited two intensity peaks signifying two hydrodynamic sizes averaging at 11 nm and 76.2 nm, respectively. The appearance of these two peaks might indicate the population of polydisperse AgNPs as a consequence of the growth and aggregation of AgNPs. There is also a possibility that these two peaks signify the presence of rod-like structures nanoparticles diffusing the aqueous media as similar DLS profiles were observed for silver and gold nanorods, as reported in previous studies [24-26]. However, information from both UV-Vis and DLS characterizations were insufficient to confirm the definite structure obtained from the nanoparticle’s nucleation and growth.

Figure 2. DLS result of the PVP-capped AgNPs synthesized using 0.001 M and 0.02 M of silver precursor.

The chemical composition of the AgNPs was investigated using FT-IR spectroscopy, as presented in figure 3. For comparison, the FT-IR spectra of the PVP-capped AgNPs at varied silver precursor concentrations (0.001 M and 0.02 M) were shown with that of the PVP. Transmission bands at 2954 cm\(^{-1}\), 1428 cm\(^{-1}\), 1281 cm\(^{-1}\), and 1073 cm\(^{-1}\) appeared in the spectrum of the pure PVP sample, corresponding to the characteristic vibrations of CH\(_2\), C-H, N-O, and C-N stretchings respectively, typical for PVP [27, 28]. A strong band at 1655 cm\(^{-1}\) also appeared, indicating the presence of the carbonyl group present in the structure of PVP [27]. Interestingly, these bands were manifested in both AgNP samples, suggesting the successful incorporation of PVP on the AgNP structures. Furthermore, the shifting and broadening of the transmission bands of the C=O at 1655 cm\(^{-1}\) for PVP (in blue) to 1680-1683 cm\(^{-1}\) for that of PVP-capped AgNPs (in black and red) might suggest the formation of linkages between the AgNPs and C=O group. It was also observed that the band at 1281 cm\(^{-1}\) for PVP disappeared in both AgNP samples indicating the interaction between the AgNP to the nitrogen-containing group. This was followed by the shifting and strengthening of bands at 1059-1079 cm\(^{-1}\) for AgNPs samples, that suggest strong coordination between AgNPs and N atoms [29]. According to previous reports, coordination of AgNPs was typically observed at the oxygen and/or nitrogen sites highly available in the chemistry of PVP [28-30]. In general, there was no significant difference between the spectra of PVP-capped AgNPs synthesized at 0.001 M and 0.02 M precursor concentration. However, there was an observed difference in the intensity of their transmission bands that might suggest a difference in the amount of functional groups coordinated on the AgNP surface.
Figure 3. FT-IR spectra of the PVP and PVP-capped AgNPs produced using 0.001 M and 0.02 M precursor concentration.

A sample TEM image and size histogram of the PVP-capped AgNPs derived using low precursor concentration is shown in figure 4. The formation of spherical AgNPs was evident with a mean diameter of 14.67 ± 3.85 nm. As expected, this value was smaller with respect to the DLS result since TEM cannot detect the polymeric PVP that capped the AgNPs that was detected by the DLS technique [31]. Upon closer inspection, a rod-like growth of the nanoparticles was observed. This might suggest that the formation of rod-like or elongated nanostructures was favoured in this synthesis route and addition of more silver ions to supply the nanoparticle growth may lead to the formation of non-spherical AgNPs [32-33]. It has been reported that several nanoparticles with non-spherical structures such as nanorods were obtained in the presence of PVP [33-35]. Accordingly, the strong binding of action of PVP effectively controls the growth of nanoparticles. The growth of crystallite faces where PVP were attached becomes limited while faces with minimal linkages of PVP have grown freely leading to the anisotropic growth of the nanoparticles [36-38].

Figure 4. (a) TEM image of PVP-capped AgNP (inset shows the magnified image of the AgNPs) and (b) histogram of the AgNP diameter size.
4. Summary and conclusion
A successful synthesis of PVP-capped AgNPs was presented via chemical reduction of silver ions in the presence of sodium borohydride and sodium citrate as co-reducing agents. Control on the optical absorbance of PVP-capped AgNPs was demonstrated by the shifting and broadening of absorbance peaks at around 401 nm to 530 nm as we vary the concentration of silver precursor. AgNPs synthesized from low precursor concentration (0.001 M) produced a narrow and symmetric absorbance peak while high precursor concentration (0.02 M) produced a broad and asymmetric peak. DLS result of the PVP-capped AgNPs from low precursor concentration revealed hydrodynamic size average at 21.10 nm with a good dispersity (PDI = 0.264) while PVP-capped AgNPs derived from high precursor concentration exhibited two intensity peaks signifying two hydrodynamic size population averaging at 11 nm and 76.2 nm, respectively. Finally, the TEM image exhibited the presence of spherical AgNPs showing good dispersity with an average size of 14.67 nm ± 3.85 nm. Subsequent formation of rod-like AgNPs nanostructures was also noticed. This paper presented a valuable insight for tuning the properties of AgNPs for future practical applications.

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