Facile Synthesis of Monodispersed Ag NPs in Ethylene Glycol Using Mixed Capping Agents

Suyue Chen, Jacob R. Drehmel, and R. Lee Penn*

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ABSTRACT: Capping agents play an important role in the synthesis of silver nanostructures in polyol solvents. In this work, we demonstrate that using a small amount of tannic acid (TA), a reducing capping agent, in addition to poly(vinylpyrrolidone) (PVP), a protective capping agent, can lead to the production of monodisperse spherical silver nanoparticles (Ag NPs) that are stable with respect to particle aggregation for at least 100 days and have particle sizes ranging from 16 to 28 nm depending on the TA concentration. We hypothesize that the complexation between PVP and TA can lead to the formation of a stable particle coating and a fast Ag+ reduction rate at a relatively high TA concentration. Both effects can benefit the formation of small spherical Ag NPs with narrow size distribution.

INTRODUCTION

Silver nanostructures, such as nanoparticles (NPs) and nanowires (NWs), have found use in a wide range of applications, such as in transparent electronic devices,1−3 biosensors,4,5 and photovoltaic and photocatalytic devices.6,7 Stable and monodisperse Ag NPs are desired in many applications.8 The focus of this study is to prepare such particles using the polyol synthesis method, which is simple to perform and scalable and has been shown to produce a wide variety of silver nanostructures.9,10

Capping agents play an important role in controlling the shape and size of silver nanostructures produced in polyol reactions. The preferential adsorption of capping agents onto specific silver crystal facets can serve to control both the size and shape of silver nanocrystals. For example, poly-(vinylpyrrolidone) (PVP) is a commonly used capping agent, and it preferentially adsorbs onto (100) silver crystal surfaces over (111) facets, which can facilitate the growth of Ag NWs.11,12 Some capping agents can also serve as reducing agents, and the rate of reduction can be controlled by varying concentration and temperature. For example, tannic acid (TA) and citrate are two capping agents that can also reduce Ag+ to Ag(0) and have been employed in successful syntheses of silver nanostructures in both water and polyol solvents.13−18

Furthermore, using a capping agent that can serve as a reductant in addition to a protective capping agent in a single reaction may lead to the size-controlled synthesis of monodisperse Ag NPs that are stable in suspension for long periods of time. In the work reported by Bastús et al., sodium citrate and a small amount of TA were used together in the aqueous synthesis of Ag NPs.15 In their reaction, TA induced fast Ag+ reduction at the early stage of the reaction to produce a large number of nuclei, which led to the formation of small monodisperse particles. The particle size can be controlled by TA concentration. The citrate ions effectively capped the Ag NP surfaces, and the resulting Ag NPs were free from aggregation for over 49 days.15

In this work, we report the production of stable monodisperse Ag NPs produced by using both TA and PVP in polyol. In addition to the synergy described above, the complexation between TA and PVP may improve the stability of the nanoparticles against aggregation at a relatively low PVP concentration. The PVP−TA complexation might also suppress TA−Ag+ chelation, which could allow for the fast production of small Ag NPs at higher TA concentrations.

RESULTS AND DISCUSSION

Monodisperse and stable dispersions of Ag NPs were produced using a polyol-based synthesis method with a mixture of two capping agents, PVP and TA (Figure 1). Figure 1 shows UV−vis spectra, representative transmission electron microscopy (TEM) images, and size distributions of Ag NPs produced in ethylene glycol using 1 mM PVP and 5−1000 μM TA. The TEM images demonstrate a narrow size distribution when the TA concentration is between 50 and 150 μM. The UV−vis spectra of Ag NP suspensions produced using TA concen-
trations of 150 μM or lower have single absorbance peaks that are relatively narrow, which also suggest monodisperse particle sizes.19,20 In addition, the product Ag NPs appear to have uniform coatings in TEM images, with an average thickness of ca. 2–3 nm. Such synthesis using mixed capping agents could be readily reproduced, with four trials of the reaction using 100 μM TA exhibiting UV–vis absorbance peak shapes and widths of the as-prepared product suspensions using PVP alone as compared to using both PVP and TA (Figures S1 and S3) suggest that both conditions can produce Ag NPs with narrow size distributions. However, after particle separation and washing, substantial particle aggregation was observed in dispersions of Ag NPs produced from polyol reactions without the addition of TA (Figure 2). In contrast, Ag NPs from PVP–TA reactions had monodispersed size distributions, as can be seen in the TEM images and histograms of Figure 1. In fact, both PVP and TA were detected in Ag NP samples collected from PVP–TA syntheses via infrared spectroscopy (Figure S4). The characteristic peaks of both PVP and TA were observed. These data suggest that the coating produced in solutions containing the PVP–TA complexes is more effective in preventing aggregation as compared to that from PVP of similar concentrations.

We hypothesize that the formation of small spherical Ag NPs with narrow size distribution is facilitated by the complexation of PVP and TA.21 The spontaneous formation of particles in solutions containing TA and PVP can be demonstrated by a simple, qualitative light scattering test, in which a red laser is shined through the EG mixtures containing PVP, TA, or both PVP and TA (Figure S2). At room temperature, mixtures containing 1 mM PVP (by repeat unit) and TA at a concentration higher than 5 μM showed significantly stronger light scattering than the mixtures containing PVP or TA alone, suggesting the formation of PVP–TA particles. These particles may result from the exothermic PVP–TA complexation described by Bizley et al.21 Although light scattering decreased in all mixtures when heated to 150 °C, PVP–TA mixtures still exhibit stronger scattering than PVP or TA in EG.

The PVP–TA complexation may lead to a better coating on Ag NPs, which could inhibit aggregation as compared to using PVP alone. The similar UV–vis absorbance peak shapes and widths of the as-prepared product suspensions using PVP alone as compared to using both PVP and TA (Figures S1 and S3) suggest that both conditions can produce Ag NPs with narrow size distributions. However, after particle separation and washing, substantial particle aggregation was observed in dispersions of Ag NPs produced from polyol reactions without the addition of TA (Figure 2). In contrast, Ag NPs from PVP–TA reactions had monodispersed size distributions, as can be seen in the TEM images and histograms of Figure 1. In fact, both PVP and TA were detected in Ag NP samples collected from PVP–TA syntheses via infrared spectroscopy (Figure S4). The characteristic peaks of both PVP and TA were observed. These data suggest that the coating produced in solutions containing the PVP–TA complexes is more effective in preventing aggregation as compared to that from PVP of similar concentrations.

The PVP–TA complexation may also influence the rate of Ag⁺ reduction. It has been demonstrated that fast Ag⁺ reduction at the early stage of reaction can lead to the production of smaller spherical Ag NPs with narrow size distribution and slow reduction of larger Ag NPs.22 TA can induce two opposing effects on the reaction kinetics: (1) TA is a reducing agent and can accelerate Ag⁺ reduction,23 and (2)
TA can chelate Ag⁺ and lower the free Ag⁺ concentration in solution, which would decelerate Ag⁺ reduction. For example, polyol reactions performed using TA without the addition of PVP were sensitive to TA concentration (Figure 3).

Monodisperse Ag NPs were produced when using 1 or 10 μM TA (TA/AgOCOCF₃ molar ratios at 1:30 and 1:3, respectively; Figure 3a,b). However, the higher concentration of 100 μM and 1 mM TA led to Ag NPs with heterogeneous shapes and wide size distributions (Figure 3c,d). The broadened particle size distribution can be explained by the slower Ag⁺ reduction, which was presumably caused by TA–Ag⁺ chelation, and similar results are reported in the literature for aqueous Ag NP synthesis using TA.²³,²⁴

PVP–TA complexation may suppress the chelation of Ag⁺ by TA and accelerate Ag⁺ reduction when PVP and TA are both present. This can explain the decreasing particle size observed at higher TA concentrations (Figure 1). In addition, the narrower size distribution of Ag NPs is consistent with faster nucleation and slower and less subsequent growth on the higher TA concentration (TA/AgOCOCF₃ molar ratio at 3.3:1), polydisperse and aggregated Ag NPs were produced.

To track the reaction rate, UV–vis absorbance spectra of reaction mixtures were measured over time. Aliquots collected from PVP–TA reactions had narrower peak widths than observed from reactions using PVP without the addition of TA, which suggested narrower Ag NP size distributions. In addition, reactions using 1 mM PVP with 0–100 μM TA were all very rapid, and the reaction extent exceeded 70% within 1 min (Figure S5), rendering these measurements inconclusive in terms of comparing reaction rates.

To better demonstrate the effect of TA and PVP on the reaction rate at early stages, a series of scaled-up Ag NP syntheses (each with 25 mL of reaction mixture volume) were performed in 100 mL Schlenk bottles. The scaled-up reactions exhibit slower reaction rates than the aforementioned rapid reactions performed in 20 mL scintillation vials (each with 5 mL of reaction mixture volume). As compared to the scaled-up reaction using 1 mM PVP, the reaction using 1 μM TA in the absence of PVP and the reaction using 1 μM TA and 1 mM PVP were both significantly faster (Figures 4 and S6). When the TA concentrations were increased to 100 μM, the rate of both reactions decreased, which could be explained by the TA–Ag⁺ chelation. However, the reaction using 100 μM TA without the addition of PVP was significantly slower than the one using 100 μM TA with 1 mM PVP. These observations demonstrated that the PVP–TA complexation may suppress TA–Ag⁺ chelation and promote Ag⁺ reduction at relatively high TA concentrations.

TA is both a reducing agent and a chelating agent for Ag⁺. More interestingly, its complexation with PVP makes its effect more unique. The combined effect of PVP and TA influences the rate of Ag⁺ reduction at different stages of the reaction, the rate of Ag atom addition onto existing silver particles, and the aggregation of Ag NPs.

Therefore, the combined effect of PVP and TA makes the synthesis of Ag NPs in the TA–PVP system unique. Our results showed that using TA in combination with PVP in a polyol reaction may improve the size and shape control of the Ag NPs produced. A different species that is both a reducing agent for Ag⁺ and a capping agent of Ag NPs would have a different effect on the reaction when used together with PVP. For example, citrate is another commonly employed reducing capping agent in Ag NP syntheses in EG,¹¹,²⁵ but it neither forms a complex with PVP nor forms a chelate with Ag⁺ in the same way as TA. Indeed, Ag NP syntheses using PVP and citrate with similar conditions as the PVP–TA reactions resulted in particles with poor size and shape control (Figure S7).
Moreover, the wide range of optimal TA concentration in our PVP–TA method can be an advantage. When using the monodisperse Ag NPs as seeds for additional silver growth, it is beneficial to directly use the as-prepared particle suspension since separating and washing the Ag NPs may compromise their reactivity in the growth reaction. A wider optimal concentration range leaves more room for the choice of seed growth reaction conditions.

**CONCLUSIONS**

This work employed a combination of protective and reducing capping agents in the synthesis of Ag NPs in EG: PVP and TA. Reactions using both PVP and TA produced stable monodisperse Ag NPs with better size and shape control as compared to using TA or PVP alone. The PVP–TA synergy observed may be the result of complexation between PVP and TA, which enhances Ag NP protection and facilitates control over the reaction rate. The PVP–TA reaction system also has a relatively wide range of optimal TA concentration, which provides a handle for size control and could be beneficial for using the Ag NPs in seeded silver nanocluster syntheses. Similar strategies using mixed capping agents may be applied in the colloidal syntheses of varied metal nanoparticles.

**EXPERIMENTAL SECTION**

**Chemicals and Instruments.** Chemicals used in this study included MilliQ Water (using Millipore, 18.2 MQ), ethylene glycol (EG, ACS certified, Fisher Chemicals), silver trifluoroacetate (AgOCOCF₃, 98%, Sigma-Aldrich), poly-(vinylpyrrolidone) (PVP, Alfa Aesar, M.W. 1 300 000), sodium citrate dihydrate (ACS reagent, Macron), and tannic acid (TA, ACS reagent, Sigma-Aldrich). Solvents and chemicals were used as received. Silver trifluoroacetate solutions were freshly prepared before reaction, during which silver salt was handled using plastic scoops.

Instruments used for Ag NP synthesis included a magnetic stir plate, 20 mL scintillation vials, a 100 mL Schlenk bottle, an argon purging gas line, a heating mantle, and a temperature control unit composed of an Omega PFA-coated 12° type J thermocouple and an NI USB-TC01 thermocouple measurement device. All glassware was cleaned by submerging in a 4 M HNO₃ solution for at least 8 h, rinsed using MilliQ water, and then dried before use.

**Reaction Procedures and After Treatments.** The Ag NP syntheses using various PVP, TA, and sodium citrate concentrations were performed in 20 mL scintillation vials under argon. In each reaction vial, appropriate volumes of EG, PVP in EG, TA in EG, and sodium citrate in EG (Table S1) were added to make EG solutions with a total volume of 4.9 mL. With magnetic stirring, the reaction mixtures were heated to 150 °C and held at that temperature for 30 min under an argon atmosphere. Then, 100 μL of 1.5 mM AgOCOCF₃ in EG was injected, resulting in a 5 mL reaction mixture with an Ag⁺ concentration of 30 μM, as well as the desired PVP and TA concentrations. The reaction mixture was heated at 150 °C for another 1 h before cooling by submersion of the reaction vessel in an ice bath. For reaction rate measurements, the vessels were held at 150 °C for various times after AgOCOCF₃ injection and immediately followed by cooling in an ice bath.

To separate the particles from a reaction mixture and prepare samples for transmission electron microscopy (TEM), 500 μL of the reaction mixture was mixed with 1.5 mL MilliQ water. The resulting mixture was centrifuged (16 500g for 40 min), and the supernatant was discarded. The particles were then resuspended in 1 mL MilliQ water and centrifuged again (16 500g for 40 min). Finally, the particles were resuspended in 20 μL MilliQ water, dropped onto a holey-carbon-coated copper TEM grid, and dried in air.

A series of scaled-up Ag NP syntheses were performed in 100 mL Schlenk bottles under argon. In each reaction, appropriate volumes of EG, TA in EG, and PVP in EG (Table S2) were added to make a solution with a total volume of 24.5 mL. With magnetic stirring, the reaction mixture was heated to 150 °C and held at that temperature for 30 min under an argon atmosphere using an argon purging gas line (not a Schlenk line). Then, 500 μL of 1.5 mM AgOCOCF₃ in EG was injected, resulting in a 25 mL reaction mixture with a Ag⁺ concentration of 30 μM and the desired PVP and TA concentrations. The reaction mixture was held at 150 °C for an additional hour before cooling by submersion of the reaction vessel in an ice bath. During the reaction, several samples (1.5 mL each) were taken from the reaction mixture at different time points after AgOCOCF₃ injection and immediately followed by cooling in an ice bath.

**Nanostructure Characterization and Analysis.** UV–vis spectra were obtained from as-synthesized product mixtures using an Agilent 8453 UV–vis system. An FEI Tecnai T12 transmission electron microscope was used to collect TEM images of Ag NPs. The Ag NP diameters were measured from the TEM images, and the coating layer thickness was calculated by \((d_{\text{total}} - d_{\text{Ag}})/2\), in which \(d_{\text{total}}\) is referred to the total diameter of Ag NPs, including the coating layer, and \(d_{\text{Ag}}\) is the diameter of the Ag NP core. Figure S1d shows a zoomed-in TEM image illustrating how the polymer coating on Ag NPs can be observed in TEM images. All size measurements were conducted manually in TEM images using ImageJ.29

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04492.

Additional synthesis formulation details including the amounts of capping reagents; UV–vis spectra of as-prepared reaction mixture and after 100 days of storage at ca. 4 °C; TEM images of Ag NPs collected from polyol reactions; photographs of reaction mixtures during the laser scattering test; FTIR spectra of Ag NPs with different organic coating; and reaction extent analysis plot over time for polyol reactions (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

R. Lee Penn — Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States; orcid.org/0000-0002-9610-9507; Email: rleeppen@umn.edu

**Authors**

Suyue Chen — Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States; orcid.org/0000-0002-5672-7212

Jacob R. Drehmel — Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United States

Complete contact information is available at: https://dx.doi.org/10.1021/acsomega.9b04492

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