

Synthesis of Silver (nano)Particle under Hyperbranched Poly(amido amine)s

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ABSTRACT: Ag colloidal particles stabilized by poly(*N,N'*-methylene bis-acrylamide *N*-aminoethyl piperazine) (MBA-AEPZ) were prepared. The Ag⁺ ion concentration and reaction temperature were studied on the size and size distribution of Ag colloidal particles, which were determined from the ultraviolet (UV) plasmon absorption band and transmission electron microscopic (TEM) analyses. The data show that poly(MBA-AEPZ) behaves like lower molec-

ular mass stabilizers; some polymers surround the surface of the Ag colloidal particles and the particle size can be controlled by a change in the Ag⁺ ion concentration and reaction temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3701–3705, 2007

Key words: synthesis; silver particle; poly(*N,N'*-methylene bis-acrylamide *N*-aminoethyl piperazine); TEM

INTRODUCTION

Metal nanoparticles have unique properties that result from size effects. Control of the size of particles through reducing the surface energy by means of the adsorption of stabilizers such as polymeric ligands or surfactants is an important research area in nanoscale science and engineering.^{1,2} Recently, colloidal metal nanoparticles protected by dendrimers have received much attention, since dendrimer molecules with a well-defined structure can be used as templates in inorganic nanoparticles.^{3–7} At the same time, some work has demonstrated the concept that larger metal particles (2–3 nm) can be protected by the exterior amine groups of dendrimers that act, for the most part, as stabilizers.^{8–10} The studies of Manna et al.¹¹ have refined this model, and very stable silver nanoparticles surrounded by the terminal amino groups of dendrimers have been prepared successfully, as Crooks and Esumi demonstrated.^{7,8} Hyperbranched polymers are expected to be more attractive in practical applications¹² used to protect metal nanoparticles because their structure is also easy to control, as well being able to efficiently control the synthesis of Ag nanoparticles. Here, the hyperbranched polymer of poly(*N,N'*-methylene bis-acrylamide *N*-aminoethyl pi-

perazine) (MBA-AEPZ) was synthesized and its effect on the preparation of Ag nanoparticles was studied.

EXPERIMENTAL

Materials

N,N'-methylene bis-acrylamide (MBA, 99.9%) and *N*-aminoethyl piperazine (AEPZ, 99.9%) were purchased from Aldrich Chemical (Milwaukee, WI). Silver nitrate (AgNO₃, 99.99%) and sodium borohydride (NaBH₄, 99%) were also purchased from Aldrich Chemical.

Synthesis and properties of the hyperbranched polymer of poly(MBA-AEPZ)

When the feed ratio of MBA to AEPZ was 2 : 1, a typical polymerization procedure was as follows: 4 mmol MBA was added to a solution of 2 mmol AEPZ and 4 mL mixture solution containing 70% methanol and 30% water (v/v). The polymerization was performed at 50°C for 6 h. Then the polymerization was stopped and the solution was concentrated under reduced pressure, followed by precipitation in cold acetone. The product was purified by dissolving in water and precipitating in cold acetone again. The procedure was repeated three times. The product was then dried under vacuum at 40°C for 24 h. The structures of the hyperbranched poly(amido amine)s are shown in Figure 1 and verified by ¹³C-NMR. a3 (50.0–51.0 ppm, 1C), b3 (54.0–55.0 ppm, 1C), c3 (52.0–52.5 ppm, 1C), d3 (51.5–52.0 ppm, 1C), e3 (52.5–53.0 ppm, 1C), f3 and h3

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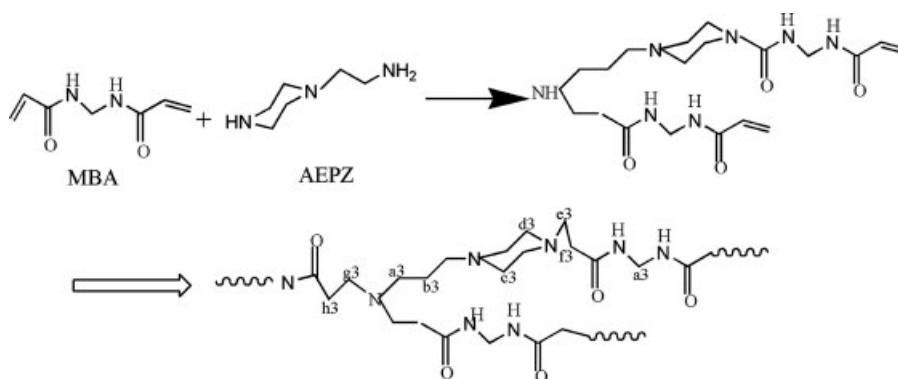


Figure 1 Scheme representing the synthesis of a hyperbranched polymer.

(32.0–33.0 ppm, ^{2}C), g3 (53.5–54.0 ppm, ^{2}C), m3 (44.0–45.0 ppm, ^{12}C or ^{13}C). Its molecular weight (M_w) and distribution (M_w/M_n) were 1432 and 1.53, respectively.

Synthesis of Ag particles protected by the hyperbranched polymer

The synthesis procedure was similar to that reported in the literature.¹³ The hyperbranched polymer aqueous solution and AgNO_3 aqueous solution were mixed together to produce a reaction mixture. The NaBH_4 aqueous solution was slowly dropped into the reaction mixture while stirring. The reaction mixture turned to a yellow or brown color within a few seconds after the addition of the first drop of the NaBH_4 solution. The stirring was continued for 2 h to complete the reaction. Finally, we obtained a yellow or brown colloidal solution of hyperbranched polymer-protected particles. The hyperbranched polymer-protected particles were very stable in aqueous and methanol solution at room temperature for 2 months.

Methods and measurements

Optical measurements were carried out at room temperature on a Shimadzu UV 2200 UV-vis spectrome-

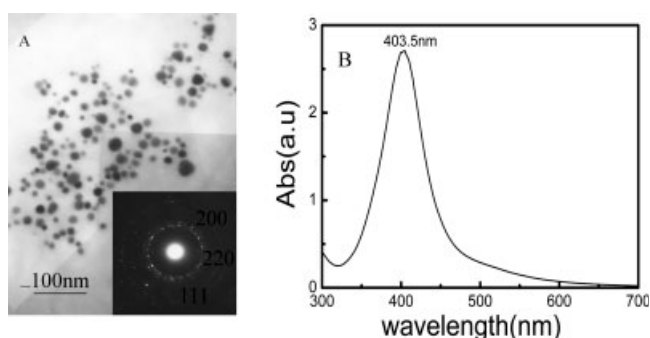


Figure 2 (A) TEM image and (B) UV spectrum of polymer-protected Ag nanoparticles. Its electron diffraction is shown in the inset.

ter using a quartz cell (10 mm path). The size and morphology of the particles were observed at room temperature with a Hitachi H-800 electron microscope operating at 100 kV. The size distribution was derived from histograms.

RESULTS AND DISCUSSION

Formation of Ag nanoparticle encapsulated Poly(MBA-AEPZ)

Ag colloidal nanoparticles can be prepared in the presence of Poly(MBA-AEPZ), as shown in Figure 2. As shown in Figure 2(A), the particles are spheres, sizes ~ 10 nm. A typical electron diffraction pattern image is shown in the inset of Figure 2(A), which shows growing parallel to the (111), (200), and (220) planes of cubic silver, indicating the formation of Ag nanoparticles. A dilute Ag colloidal solution prepared in an M : D ratio (0.017 : 1) and at 25°C displayed a strong absorption in the 403.5 nm region [Fig. 2(B)]. This peak must arise from the surface plasmon

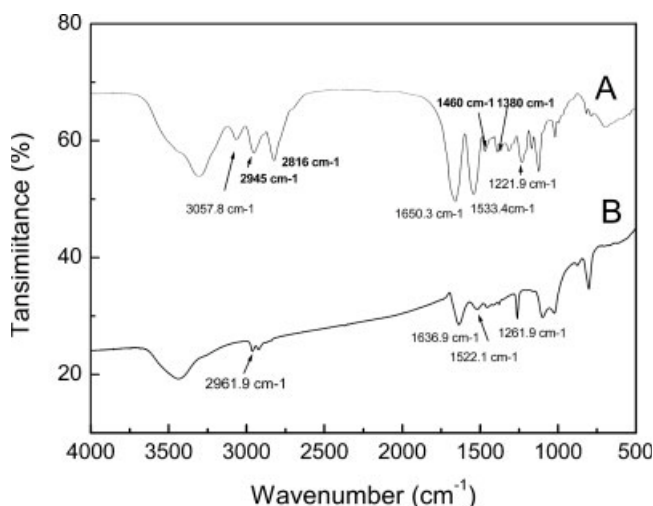


Figure 3 FT-IR spectra of (A) free poly(MBA-AEPZ) and (B) Ag nanoparticles coated with poly(MBA-AEPZ).

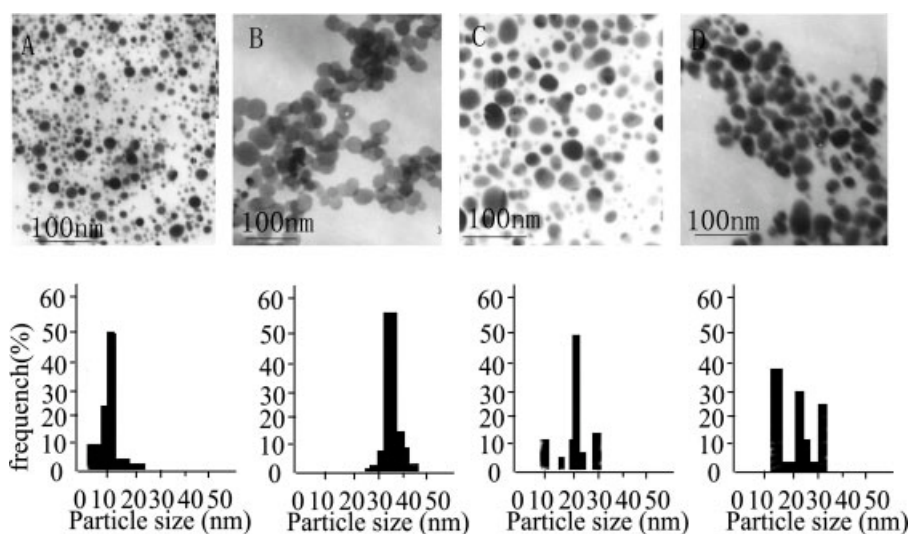


Figure 4 TEM images of Ag colloidal nanoparticles prepared in various M:D ratios of (A) 0.003 : 1, (B) 0.006 : 1, (C) 0.008 : 1, and (D) 0.009 : 1, corresponding to size distributions as well.

absorption of the silver clusters^{14,15} (which further confirms the formation of Ag nanoparticles). The electronic energy levels and optical transition in a "roughened" Ag surface had been extensively studied and it had been confirmed that the 4d to 5sp interband transition generally occurs at around an energy corresponding to 320 nm (i.e., 3.8 eV).¹³ The characteristic plasmon absorption band around 403.5 nm supported the formation of "quantum-dot" particles,¹⁶ suggesting Ag nanoparticles protected by Poly(MBA-AEPZ).

Figure 3 shows a comparison of the FT-IR spectra between 4000 cm^{-1} and 700 cm^{-1} of free Poly(MBA-AEPZ) and Poly(MBA-AEPZ) protecting particles, suggesting further the Ag colloidal nanoparticles protected by Poly(MBA-AEPZ). The similarity of the features of these two spectra confirm 1) the polymer as an essential component of the composite nanoparticles, and 2) the polymer molecule was not removed after washings of the precipitate. The bands at 3057.8 cm^{-1} and 2945.0 cm^{-1} correspond to the amide A (as shown in Fig. 1). An observation of the spectra shows that the amide stretching frequencies disappear and shift to higher regions (to 2961.9 cm^{-1}) after the adsorption of the Ag particles. The characteristic bands assigned to amides I, II, and III are at 1650.3, 1533.4, and 1221.9 cm^{-1} , respectively. The amide I and II bands shift to slightly lower (1636.9 and 1522.1 cm^{-1} , respectively) regions. However, amide III shifts to higher (1261.9 cm^{-1}) regions with respect to the adsorbed situation. All of these amines stretching vibration frequencies changes indicate that the Ag nanoparticles were protected by the Poly(MBA-AEPZ) through the interaction between Ag and the exterior and inside amine group of Poly(MBA-AEPZ), which is different from previous results.⁸⁻¹⁰

Effects on silver particle sizes and size distributions

Size and size distributions of dependence on M : D ratios

The size and size distribution of the particles prepared using the Poly(MBA-AEPZ) at different M : D ratios were examined by TEM, as shown in Figure 4. The size of the particles as a function of the M : D ratio used to synthesize them is summarized in Table I. The values of UV are also included in Table I. This shows that the average particle size increases at first, with an increase in the M : D ratio, and rapidly decrease with further increasing the M : D ratio, which is in agreement with our UV experiments and the results reported by others.^{15,17,18} It can be observed that the average size of prepared particles is at least 9.7 nm, suggesting that the Ag nanoparticles form outer Poly(MBA-AEPZ) in the M : D ratio range (0.004 : 1–0.009 : 1) (Fig. 1). The result is attributed to the finding that the polymer of Poly(MBA-AEPZ) with a small hole is not enough to act as a template. At this time, the Poly(MBA-AEPZ) behaves like lower molecular mass stabilizers that stabilize particles by the exterior and

TABLE I
Characteristic Dates for Hyperpolymer Protected Ag Nanoparticles

Concentration of AgNO ₃ solution used (μM)	Ag ⁺ : NH ₂ group (M : D) ratio	λ_{max} (nm)	Average particle size (nm)
0.4	0.003 : 1	447	9.7
0.8	0.006 : 1	517	19.5
1.0	0.008 : 1	532	37.2
1.2	0.009 : 1	489	14.6

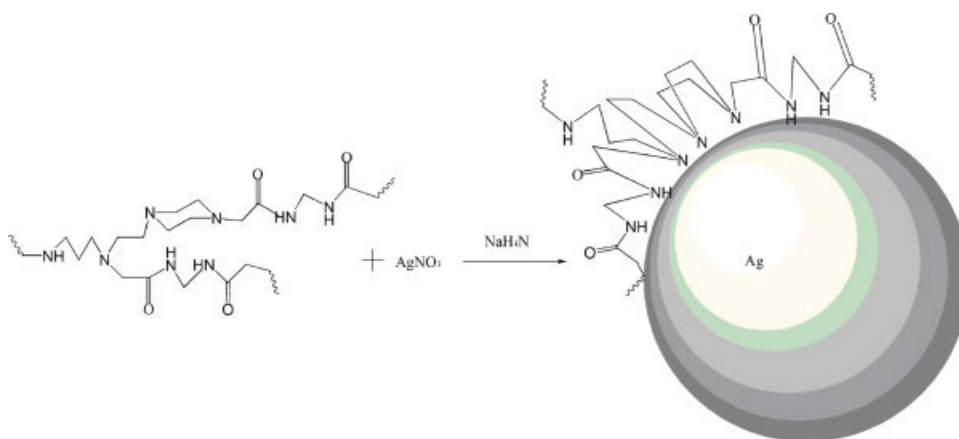


Figure 5 Scheme represents preparation of Ag nanoparticles in the presence of poly(MBA-AEPZ).

inside attachment of amine groups and some Poly (MBA-AEPZ) surround the surface of the Ag nanoparticle, as shown in Figure 5, and confirmed by FT-IR spectra (Fig. 3). As can be seen in Figure 4, the size distribution increases with increasing the M : D ratio, which results from a decrease in the number of Poly (MBA-AEPZ) stabilized per nanoparticle.

Size and size distributions of dependence on reaction temperature

The effect of reaction temperature on the size and size distribution of Ag colloidal nanoparticles was further examined, as shown in Figure 6. When the reaction temperature was set at 40°C , the nanoparticles became small and had an average size of 8.8 nm [Fig. 6(A)].

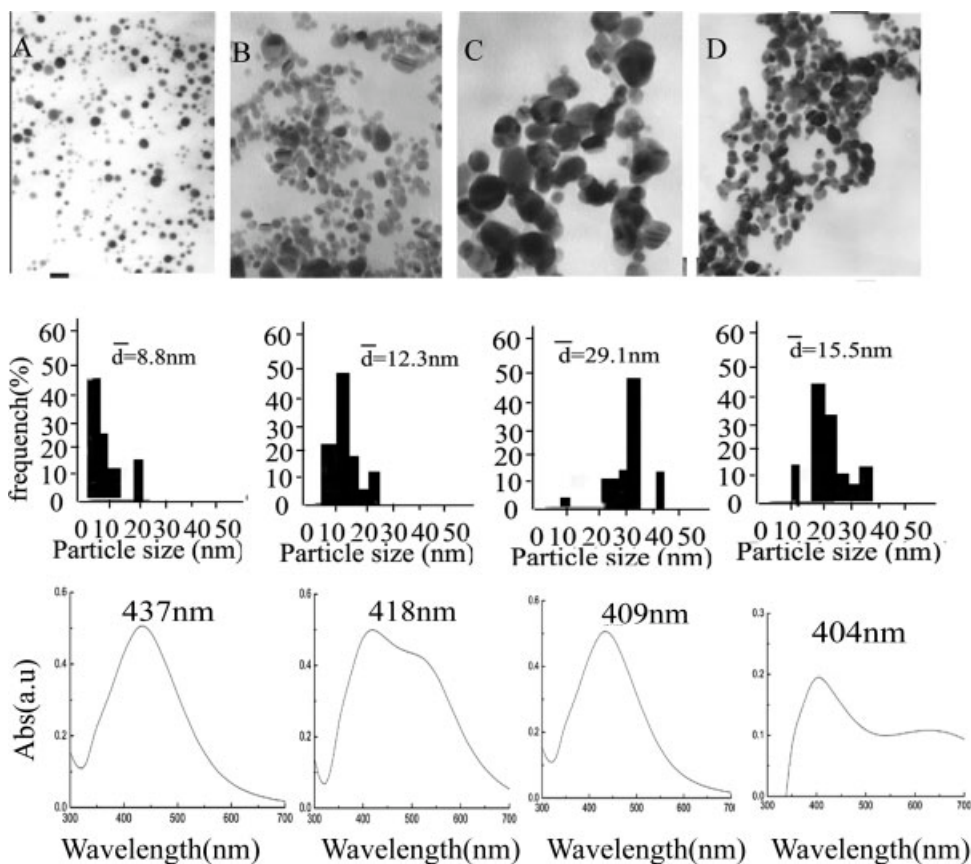


Figure 6 TEM images of Ag colloidal nanoparticles prepared at (A) 40, (B) 50, (C) 60, and (D) 70°C . The corresponding size distribution and UV spectrum are shown as well.

The higher temperature led to the continual formation of larger nanoparticles, with average sizes of 12.3 and 29.1 nm [Fig. 6(B, C)]. However, the size of particles decreased to 15.5 nm at 70°C. It is well known that the formation of small particles is kinetically favored and that the formation of large particles is thermodynamically favored. From a standpoint of kinetics, small particles are easier to nucleate. But small particles have a larger surface-area-to-volume ratio and represent a higher energy state than large particles. Hence, small particles are easily formed at lower temperature, but these small particles have a tendency to grow larger particles to attain a lower energy state when the reaction temperature is higher. As shown in Figure 6, the size distributions of the particles formed at the high temperature were relatively broadened because the interaction between NH and Ag was weak at high temperature (> 40°C). For the same reason, the change of size was inconsistent with the UV spectra (Fig. 6) because the interaction between organic molecules and particles was continually weak with increasing the reaction temperature.¹⁹ When the hyperbranched polymer was used as a disperser, reaction temperatures higher than 60°C were not able to produce stable particles. A possible reason could be the disappearance of interaction between NH and Ag. The bulkiness of the alkyl chain might prevent formation of densely packed layers on the nanoparticle surfaces that are required for the stabilization of nanoparticles. For the same reason, the size of the particles decreased rapidly to 15.5 nm at 70°C.

CONCLUSIONS

Ag colloidal nanoparticles can be synthesized in the presence of a hyperbranched polymer of Poly(MBA-AEPZ). What's more, it was found that the size and size distribution of Ag nanoparticles can be controlled with various ratios of metal ion to terminal amino groups of the polymer and various reaction temperatures. Thus, the hyperbranched polymer is

expected to prepare larger-scale size and stable metal nanoparticles displacing dendrimers. FT-IR analyses indicate that the metal particles were encapsulated by the polymer, which is different from many dendrimers and which is very important to prepare a larger-size metal (> 10 nm). Thus, a unique position may be indicated in many technological applications as a chemical sensor, in membrane chemistry, selective electrochemical reactions, and catalysis due to their capacity for high functionality and molecular-sized channels.

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