수용성 고분자를 이용한 Ag나노입자 제조 및 안정화

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Preparation and Stabilization of Silver Colloids Protected by Water-Soluble Polymers

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INTRODUCTION

Considerable attention for polymer-protected colloidal novel metal nanoparticles is currently increased since they can offer interesting optical, catalytic, magnetic, and electronic properties in technological applications. Polymer-protected metal colloids are prepared by various methods, such as chemical reductions, photoreductions, and thermal decompositions of suitable metal precursors. In this way, small particles sizes and narrow size distributions of metal particles can be obtained. However small metal particles are generally short-lived in aqueous solution as they rapidly agglomerate. Polymers as protective agent can prevent the agglomeration and the destabilization of the metal colloids during storage and use results from the repulsive interaction between polymers adsorbed to surface of metal particles. The type of the polymer influences the nanoparticle sizes and morphologies, as well as colloidal stability. Therefore, it is important to select suitable polymer for advanced stability of the metal colloid system.

Water-soluble polymers generally can be divided into two main types; ionic (polyelectrolytes) and nonionic. Polymers can be used to stabilize metal colloid either by providing electrostatic or steric repulsion. For nonionic polymers, hydration results from an interaction with a polar site in the functional group (e.g., alcohol, oxide, amide group). Then, hydrophobic groups of polymer interact with the metal colloid surface, and hydrophilic groups interact with the polar dispersion medium. In this way, nonionic polymer can stabilize metal colloid by steric effects. For ionic polymers, they can provide strong interactions with metal precursor ion by the formation of ion pairs. So they can combine both steric and electrostatic stabilization. Especially, when a polyelectrolyte is added to a suspension of particles with opposite charge, it is strongly adsorbed. That is good advantageous for obtaining small particle sizes with narrow size distribution and long-term stabilization. The charge-bearing parts in the great majority of polycationics are nitrogen based, whereas in polyanionics (polyacids), oxygen is usually involved.

Polymers can be used both to flocculate and stabilize metal colloidal dispersions. A small amount of adsorption of polymer on the surfaces of particles may permit the bridging of particles leading to flocculation. Higher amounts of adsorption lead to stabilization. If the polymer is polyelectrolyte, the adsorption of a small amount of oppositely charged polymer can neutralize the particle charge and lead to flocculation. For this reason, it is necessary to be cautious about the addition of polymer to metal colloid. Commonly, when polymer concentration is high, it tends to stabilize colloid dispersion.

In this study, we prepared polymer-protected silver colloids from silver nitrate by reduction with sodium borohydride in aqueous medium and investigated for stability of silver colloid depending on the type of protective polymer. The particle sizes and size distributions of the silver nanoparticles were determined by transmission electron microscopy (TEM), and UV-vis spectroscopy was employed for dispersion stability and additional characterization. Finally, the ability of each protective polymer to stabilize metal colloids were investigated and compared to one another.

EXPERIMENTAL

A. Materials

Silver Nitrate (AgNO3, KOJIMA Chemicals, Japan, 99.9%) as a precusor and Sodium Borohydride(NaBH4 , Aldrich) as a reducing agent were used as received to prepare silver colloid. Nonionic polymers and polyacid/polyelectrolyte used as a protective agent. Polyvinylpyrrolidone(K-15) was obtained from JUNSEI, Japan. Polyacrylamide(50wt.% solution in water), poly(sodium 4-styrene sulfonate)(20wt.% solution in water) and poly acrylic acid(sodium salt) were purchased from Aldrich. The chemicals were used as received without further purification. Deionized water(electrical resistivity 18.2MΩ) from a Millipore(Milli-Q) system was used in all preparations.

B. Preparation of silver colloid

Aqueous silver colloid was prepared by reducing silver nitrate with sodium borohydride. The redox reaction can be written as ;

$$2AgNO_3+2NaBH_4+6H_2O \rightarrow 2Ag+2NaNO_3+2H_3BO_3+7H_2$$

An aqueous solution containing the polymer(0.70wt.%, 60ml) and an aqueous solution containing silver nitrate(0.01M, 10ml) were mixed, resulting in a total solution of 90ml. This resulting solution was stirred for 30 min and then reduced at 2-3 C upon addition of aqueous solution of NaBH4(0.02M, 30ml). The reaction solution turned immediately colorless to dark brown or reddish brown(depending on the polymer).

C. Stability of silver colloid

To evaluate a stability of silver colloid, samples were exposed to UV light (4W-254nm tube). Then, the reduction rate of absorbance maximum peak with irradiation time was measured by UV-visible spectroscope (Scinco CO. LTD. S-2150). A high reduction rate indicates low dispersion stability of silver colloid.

D. Morphology and size of Ag particles

The morphology and size of particles were investigated by transmission electron microscopy(TEM, Jeol-model JEM-2000EXⅡ). A drop of dispersed samples was placed on the carbon coated TEM grid.

RESULTS AND DISCUSSION

A. Characterization of silver colloid.

The UV-visible spectrum of Ag colloids are shown in table 1 and figure 1. The UV-visible spectra show typical plasmon absorption bands for silver colloids, located at around 390-410nm. The absorbance pattern of UV-visible spectrum correlates with the size and size distribution of Ag paricles in the colloid. The narrow peak indicates narrow particle size distribution and shifts to longer wavelengths(red shift) usually means that the particle size larger. In the cases of poly(sodium 4-styrene sulfonate), the spectrum consisted of a very narrow and intense plasmon absorption band at 398nm. In contrast, for polyvinylpyrrolidone, very broad and weak absorption band was obtained Thus, it can be inferred that the Ag particles protected by poly(sodium 4-styrene sulfonate) would be minimum size and narrow size distribution.

B. Stability of silver colloid protected by polymer

In the case of reduction in aqueous phase, the prepared Ag particles were immediately precipiated and slowly formed very large agglomerate with gray color because of their hydrophobic nature. Polymer can prevent this phenomena. However different stability was observed depending on polymer type. In our experiment, the UV irradiation of the sample stimulated the aggregation and destabilization of Ag colloid protected by polymer. In figure 2. in the case of polyvinylpyrrolidone and poly(sodium 4-styrene sulfonate), high the reduction rate of the absorbance maximum peak was observed. This result might be caused by the hydrophobic character of these polymers.

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Table 1. UV-visible Spectrum Data for Ag Colloids Protected by Polymers

Protective Polymer	Type	Mw	Colloid Color	λ_{max}(nm)	FWHM(nm)
Poly vinyl-pyrrolidone	nonionic	~ 10,000	Black	391.57	273.96
poly acryl amide	nonionic	~ 10,000	Dark Brown	412.37	129.01
poly sodium 4-styrene sulfonate	anionic	~ 70,000	Red Brown	398.50	88.54
poly acrylic acid	anionic	~ 5,100	Red Brown	405.44	110.76

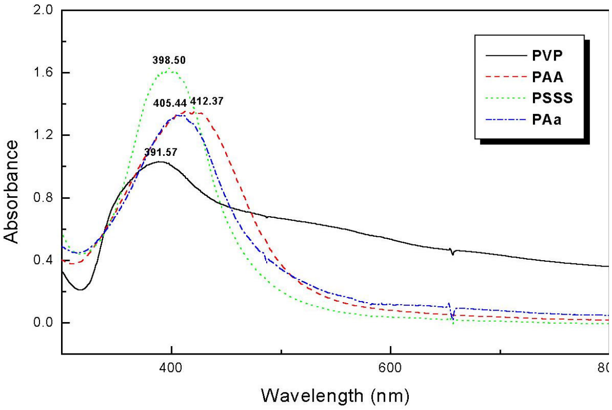

Figure 1. UV-visible Spectrum of Ag Colloids Protected by polymers

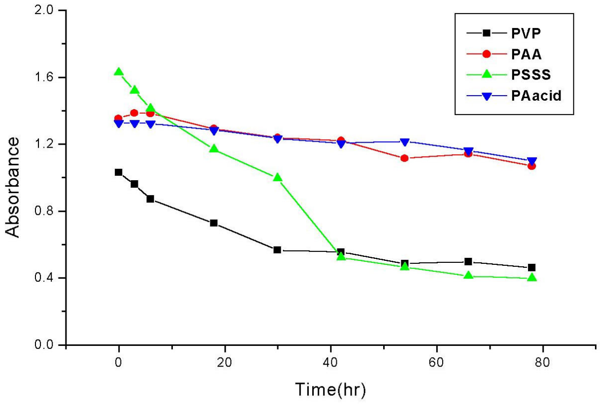

Figure 2. Absorbance maximum peak at irradiation time