

Preparation of Gold Nanoparticles in Water-Soluble Polymer Solution

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The present paper describes the effects of poly 2-vinylpyridine (P2VP) and sodium polyacrylate (PAANa) on the particle size distribution (PSD) and the formation rate of colloidal gold. Tetrachloroauric ion was only adsorbed on P2VP, which is a cationic polyelectrolyte. The anionic colloidal gold, however, was adsorbed on both P2VP and PAANa, although PAANa is an anionic polyelectrolyte. The concentration of polymer was found to affect PSD and the formation rates of colloidal gold. The addition of PAANa enables particle size to be controlled to a high degree compared with P2VP, although the adsorption of tetrachloroauric ion was not observed.

Key words: gold nanoparticles, poly 2-vinylpyridine, sodium polyacrylate, polymer adsorption

1. INTRODUCTION

Nanometer-sized particles are being investigated for applications in catalyses or optical devices, because the characteristics of these extremely small particles are different from those of bulk materials. In order to realize these applications, nanoparticles must be protected from uncontrolled aggregation. Uniform mixing and stabilization of nanoparticles is difficult, because these particles have an extremely large surface area and are quite active. Many materials have been employed for preparing and stabilizing nanoparticles, including sol-gel materials^{1,2)}, Langmuir-Blodgett films³⁾ and polymer solutions⁴⁻⁸⁾. Sol-gel materials and Langmuir-Blodgett films are suitable substrates for fixing particles but organizing particles after preparation is difficult. As such, preparation methods that use polymer solutions are often superior to other substrates. Varying the preparative condition of polymer solution enables the particle size distribution to be controlled. Furthermore, such methods allow the particles to be organized easily using an electrophoretic deposition or a self-assembly^{7,8)}, even after preparation.

In the present paper, the effects of the polymer solution on the formation and size distribution of gold nanoparticles are discussed with respect to electrostatic interaction and adsorption between polymer and gold.

2. EXPERIMENTAL

2.1 Polymers

Two kinds of water-soluble polymers were used: Poly 2-vinylpyridine (P2VP), for a cationic type polymer, and sodium polyacrylate (PAANa), for an anionic type polymer. PAANa was used as received from Polysciences Inc. The average molecular weight (Mw) of PAANa was 3,000, 20,000 or 225,000. PAANa solution was adjusted at pH = 10.5 by NaOH. P2VP (Mw = 50,000 or 200,000, Polysciences Inc.) was not subjected to further treatment, and was used as a solution, typically 1.00 g/l, at pH = 2.20 by adding HCl.

2.2 Preparation

Gold sol was produced from tetrachloroauric acid

(HAuCl₄) by 1,3-aceton dicarboxylic acid (ADCA) in the water-soluble polymer solution. First, 25 ml of 2.0 mM HAuCl₄ was mixed into 50 ml of PAANa solution under stirring at 300 rpm at 333 K. After 2 min, 25 ml of ADCA solution was added into the mixed solution, and maintained under 300 rpm mixing for 90 s. The solution initially turned gray, and then later turned red.

2.3 Characterization

Two different techniques were used to measure the size of colloidal gold in the presence of water-soluble polymer: transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS).

TEM photographs were taken at an accelerating voltage of 200 kV. Samples were prepared by placing a drop of the colloidal dispersion upon a copper grid and then evaporating the solvent.

SAXS was performed using CuK α radiation of 0.154 nm wavelength. SAXS data obtained for the colloidal gold were analyzed by the Guinier approximation method. According to Guinier's theory, the scattered intensity, $I(q)$, for a dilute system depends on the absolute value of scattering vector, q , and the radius of gyration, R_G , of the particles

$$\ln I(q) \propto -\frac{1}{3}q^2 R_G^2, \text{ where } qR_G < 1. \quad (1)$$

If the particle shape is spherical, the radius of the particle, R , is calculated as

$$R = \sqrt{5/3} R_G. \quad (2)$$

When the particles have a size distribution, the measured scattered intensity represents the sum of the scattered intensity from particles of various size, so that the estimation of particle size distribution (PSD) from the scattered intensity data is quite difficult without a preliminary knowledge of PSD formula. The formulas listed in Table 1 were tested to determine PSD, from which intensity could be fitted to the data obtained by SAXS.

UV-VIS absorbance measurements were performed at

Table 1. Particle size distributions applied for fitting of SAXS results

Log-normal distribution (LN)
$f(R) = \frac{1}{\sqrt{2\pi} \log \sigma_g} \exp\left\{-\frac{(\log R - \log R_{50})^2}{2(\log \sigma_g)^2}\right\}$
Schultz-Zimm distribution (SZ)
$f(R) = \left(\frac{z+1}{R_m}\right)^{z+1} R^z \exp\left(-\frac{(z+1)R}{R_m}\right) / \Gamma(z+1)$

wavelengths ranging from 200 to 990 nm using 5 mm quartz cell at 333 K, in order to study the reaction rates of gold ion or growth rate of gold sol.

Electrophoretic mobility measurements were performed at 298 K. The electrophoretic mobility, μ , of particles adsorbed by polyelectrolyte polymer (i.e. soft particles) is approximately given⁹ as

$$\mu = \frac{\epsilon_r \epsilon_0 \psi(0) / \kappa_m + \psi_{\text{DON}} / \lambda}{\eta} + \frac{zeN}{\eta \lambda^2}, \quad (3)$$

where $\psi(0)$ is the potential at the boundary between the peripheral zone and the medium, ψ_{DON} is the Donnan potential, κ_m is the Debye-Hückel parameter of the surface-charge layer, λ is a parameter, the reciprocal of which has the dimension of length and indicates the degree of fluid drag in the peripheral zone, η is the viscosity and ϵ_r and ϵ_0 are the relative permittivity of the medium and the permittivity of a vacuum, respectively. At the condition of high salt concentration, μ approaches a constant value given by $(zeN) / (\eta \lambda^2)$.

3. RESULTS AND DISCUSSION

3.1 Particle size distribution of colloidal gold.

A TEM photograph of colloidal gold particles prepared in the presence of P2VP is shown in Fig. 1a. Large numbers of flat triangular plates and rod-like particles were observed, the sizes of which ranged from 20 to 400 nm. When PAANA solution at pH = 2.2 was used rather than P2VP, particles of irregular shape were also obtained. Since the gold sol that was prepared in aqueous solution above pH = 4 was mostly spherical, we concluded that the hydrogen ion concentration affects particle shape.

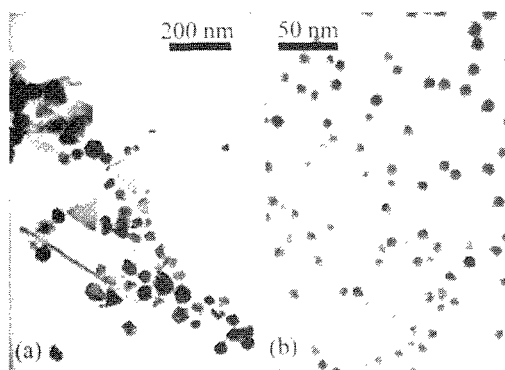


Fig. 1 TEM photographs of colloidal gold produced in the solutions containing (a) 0.01 wt% P2VP and (b) 0.40 wt% PAANA

The colloidal gold that was prepared in the presence of PAANA at pH = 10.5 was almost spherical. A TEM photograph of the typical gold sol that formed in 0.40 wt% PAANA solution is shown in Fig. 1b. The particle size distribution (PSD) of gold particles is shown in Fig. 2a. The mean particle diameter was 14 nm and the standard deviation was 3.0 nm. PSD was not symmetrical; rather, the distribution shows a precipitous rise on the small particle side and a less drastic decrease, resulting in the formation of a tail on the large particle side. Figure 2b shows the experimental scattering intensity obtained by SAXS, and the intensities calculated using the size distribution formulas listed in Table 1 and PSD measured using TEM. The calculated curve agree well with the SAXS data, due to the choice of suitable adjustable parameters. However, PSDs differed, as shown in Fig. 2a. The log-normal distribution was approximately the same as the particle size distribution measured by TEM. Therefore, we used log-normal distribution for estimating PSD from the experimental SAXS data.

Figure 3 shows the mean particle diameter, $2R_{50}$, at log-normal distribution as a function of concentration of PAANA for various average molecular weights. The mean particle size decreased as the concentration of PAANA increased.

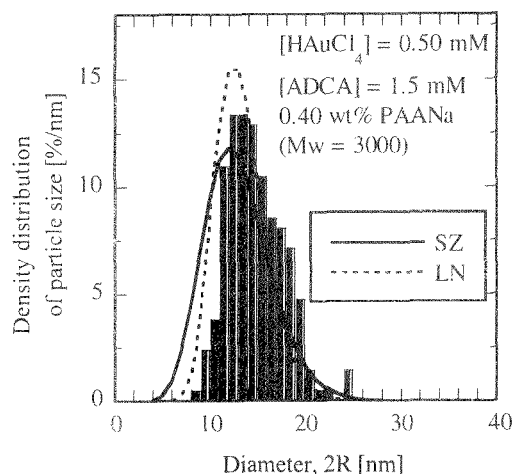


Fig. 2a Comparison of the particle size distribution obtained from TEM measurements and SAXS analysis using log-normal (LN) and Schultz-Zimm (SZ) distributions.

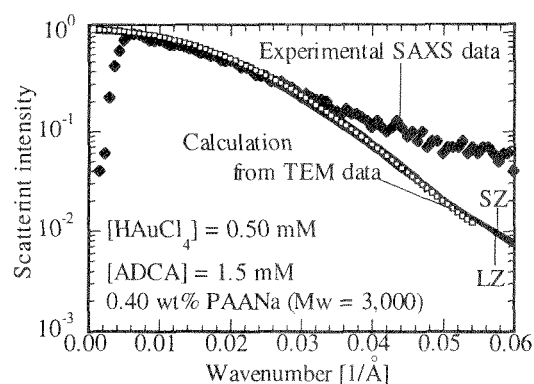


Fig. 2b Scattering intensity of SAXS.

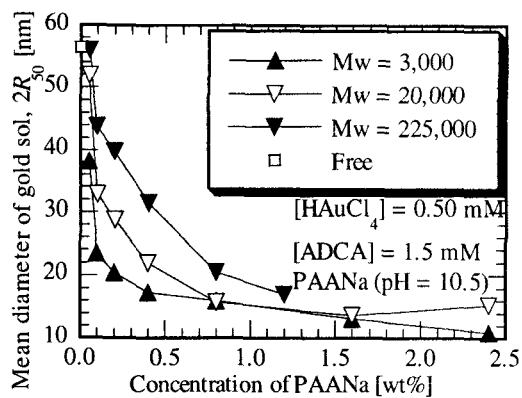


Fig.3 Relationship between mean diameter of gold sol and concentration of PAANa.

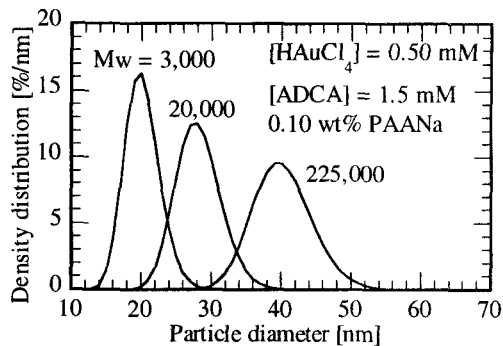


Fig.4 Effects of molecular weight of PAANa on particle size distribution at 0.10 wt% PAANa.

As compared at the same weight concentration of PAANa, the mean particle size decreased with the mean molecular weight of the polymer. Figure 4 shows the PSD of gold sol produced in 0.1 wt% PAANa of the various molecular weights. The mean particle size became smaller and the size distribution became sharper, when the polymer of lower molecular weight was used. Smaller particles having a narrower distribution were also produced at the higher PAANa concentration. Consequently, the choice of mean molecular weights and concentration of PAANa can be used to control PSD of colloidal gold particles.

3.2 Adsorption of gold ion on a polymer

The adsorption phenomena of tetrachloroauric ion on a polymer were measured by atomic absorption spectroscopy, and the results in 0.025 wt% P2VP solution and 2.4 wt% PAANa solution are shown in Fig.5. Tetrachloroauric ion was almost adsorbed on P2VP, because P2VP is cationic polyelectrolyte and tetrachloroauric ion is anionic. In contrast, PAANa adsorbed only a slight amount of tetrachloroauric ion. Since PAANa is anionic, this phenomenon can be explained by the electrostatic interaction between the polymer and the gold ion.

Figure 6 shows the electrophoretic mobility of the colloidal gold in the presence of 0.10 wt% PAANa ($M_w = 225,000$) as a function of the sodium chloride concentration at 298 K. The electrophoretic mobility increased by the addition of sodium chloride and approached a constant value. This result supports the hypothesis that the anionic PAANa adsorbed on the surface of the colloidal gold with

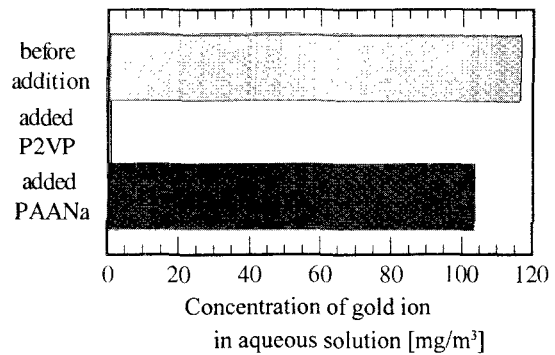


Fig.5 Adsorption of tetrachloroauric ion to polymer.

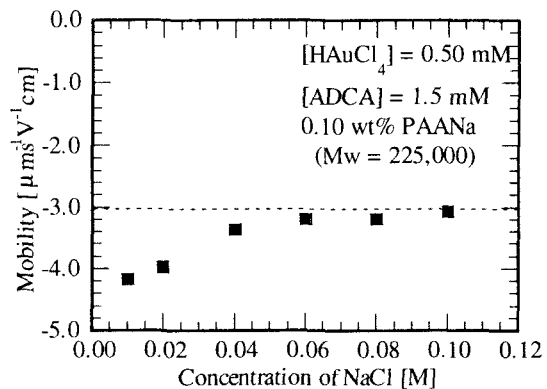


Fig.6 Electrophoretic mobility of colloidal gold as a function of concentration of NaCl.

negative charge, and the colloidal gold particles behaved as 'soft-particles'. As tetrachloroauric ion and gold particles have negative charges, P2VP may be more effective than PAANa for controlling the formation and the growth of gold particles. However, the addition of PAANa enabled wide control of particle size compared with P2VP, although the adsorption of tetrachloroauric ion was not observed. These results indicate that PAANa can control the particle size by only adsorbing on particles without the adsorption of tetrachloroauric ion.

3.3 The formation rate of colloidal gold

Light absorption due to colloidal gold sol appeared in the range of wavelengths from 510 to 570 nm. The wavelength at the maximum absorption in this range moved slightly during the reaction. At the late stage of the reaction, the wavelength of the maximum absorbance, λ_{max} , approached a constant value, which depended on the size of the gold sol. The time courses of the absorbance at λ_{max} and the gold ion concentration during the reaction are shown in Fig.7. Since these curves were similar, the formation rate of gold sol could be estimated using the absorbance at λ_{max} .

Figure 8a shows the time courses of the absorbance at λ_{max} , which represents the formation rate of colloidal gold in the presence of P2VP. The absorbance increased continuously in all cases after a certain induction period, and the formation rates were strongly affected by the concentration of polymer. Figure 8b shows the degree of adsorption of tetrachloroauric ion on P2VP. The formation rate in the presence of P2VP was slower than that in

polymer-free solution. P2VP may have prevented the colloidal gold from growing, due to the adsorption of the tetrachloroauric ion and the gold nanoparticle on the polymer.

In the case of PAANa, formation rate of gold sol was also obtained a slow, suggesting that the formation of colloidal gold was also brought about the existence of PAANa of huge molecular weight. The formation rates of gold sol, shown in Fig.9, became slower as the average molecular weights increased. The fast formation rate could be explained by the fact that PAANa composed of small molecules can diffuse faster and have a lower viscosity than the high-molecular-weight polymer.

4. CONCLUSIONS

Size control and the stability of gold nanoparticles were studied using water-soluble polymer solutions of P2VP and PAANa. Although PAANa is an anionic polymer, this polymer could be adsorbed on the anionic colloidal gold particles. The mean particle size and the size distribution of colloidal gold particles produced in a polymer solution was found to depend on the average molecular weight and the concentration of the polymer. The addition of PAANa enables particle size to be controlled to a high degree compared with P2VP due to the adsorption of colloidal gold, although the adsorption of tetrachloroauric ion to PAANa was not observed.

ACKNOWLEDGEMENTS

This work was supported in part by a grant to RCAST at Doshisha University from the Ministry of Education, Japan. YM also acknowledges Grant-in-Aid for Scientific Research (C) from the ministry of Education, Science, Sports and Culture (Grant No.10650754).

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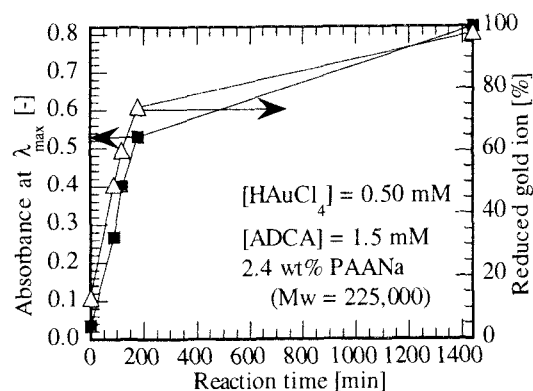


Fig. 7 Relationship between the absorbance at λ_{\max} and the ratio of the gold ion that was reduced to colloid by ADCA.

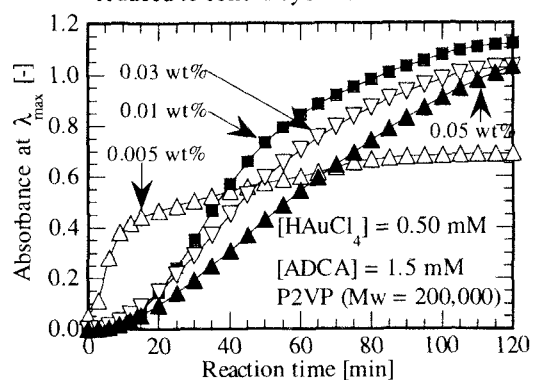


Fig. 8a Formation rates of colloidal gold in the presence of P2VP of various concentrations.

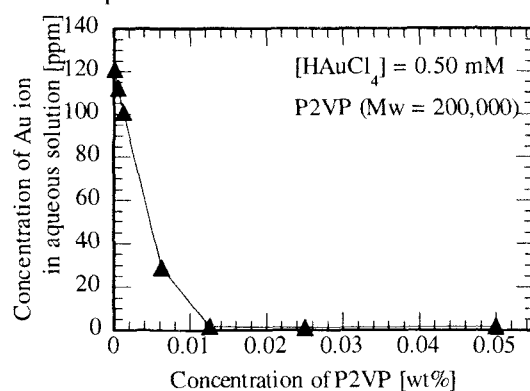


Fig. 8b Degree of adsorption of gold ion on P2VP (Mw = 200,000).

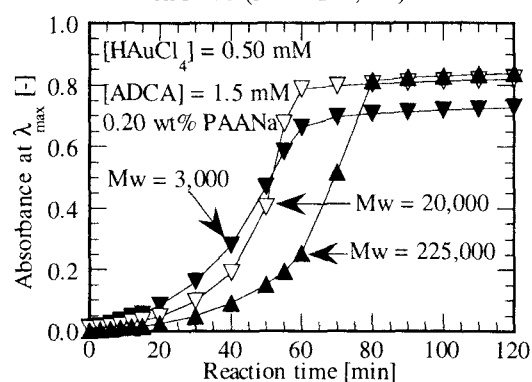


Fig. 9 Formation rates of colloidal gold in the presence of PAANa of various molecular weights.