

pH Responsive Aggregation of Imidazolium Cations-Modified Gold Nanoparticles with Poly(acrylic acid) in Aqueous Solution

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ABSTRACT: We report pH-responsive control of the colloidal dispersions of imidazolium cations-modified gold nanoparticles by using poly(acrylic acid) (PAA). The gold nanoparticles were precipitated when PAA ($M_w = 25000$) was added in aqueous solution of which pH was 2.4. The precipitate was redissolved when the solution's pH dropped below pH 1.9 and rose above pH 5.5. According to UV-visible spectra, transmission electron microscopy (TEM) observations, and dynamic light scattering (DLS) analysis, it is indicated that the gold nanoparticles at lower pH ($pH < 1.9$) were well redispersed in aqueous solution and aggregates with a diameter of 115 ± 21 nm of the gold nanoparticles were formed at above pH 5.5. Effect of molecular weights of PAA was also studied.

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KEY WORDS Gold Nanoparticle / Poly(acrylic acid) / pH-Responsive / *N*-Methylimidazolium / Nanoparticles-Based Flocculation /

Metal nanoparticles have various unusual chemical and physical properties compared with those of metal atoms or bulk metal due to the quantum size effect and their large superficial area, which make them attractive for applications such as optics, electronics, catalysis and biology.^{1,2} In recent years, controlled colloidal dispersions of the metal nanoparticles by using various stimuli, such as pH, temperature, light and so on, have been received much attention.^{3–6} Since the properties of the metal nanoparticles are largely depending on their aggregated states, a responsive aggregation system is valuable for sensing materials. In particular, pH-responsive system in aqueous solution has extremely promising prospect. Many biological phenomena, *e.g.* cellular recognition and transportation in tissues and organs, are largely concerned to pH at which they occur. There have been several reports for pH-responsive metal nanoparticles.^{7–11} Toshima and co-workers synthesized 3-mercaptopropionic acid-modified gold nanoparticles and reversibly controlled the colloidal dispersions by using interparticle hydrogen bonds or electrostatic repulsion depending on pH.⁷ Lee and co-workers synthesized gold nanoparticles coated by a hydrogel consisted of poly(acrylic acid-*co*-*N*-isopropyl acrylamide) and acted as a interrupter of surface plasmon absorbance depending on pH and temperature.⁸

Recently, we have first time prepared gold nanoparticles modified with *N*-methylimidazolium chloride (MImCl-AuNP) and reported their aggregation by anion exchange of the imidazolium salts on the surface of the gold nanoparticles.⁶ *N*-Alkylimidazolium

salts are attracting much interest in many fields of chemistry and industry as ionic liquids due to their unique properties, such as environmentally benign characteristic, highly thermal stability, non-volatile and high ionic conductivity.^{12,13} The C2 hydrogen on the imidazolium cation is acidic and an anion associates strongly to the imidazolium cation compared with a pyridinium cation or a quaternary ammonium cation.¹⁴ Here we describe pH-responsive control of the colloidal dispersions of MImCl-AuNP using a combination of poly(acrylic acid) (PAA) in aqueous solution. The strategy is based on the electrostatic interaction between the imidazolium cations on the surface of the gold nanoparticles and the carboxylate anions of PAA. There are several reports for phenomena of nanoparticles-based flocculation by charged polymers.^{15–21} Although extensive experimental and theoretical works are reported to understanding the flocculation processes and construct nanoparticles-based flocculated materials with controlled structures, studies for pH-responsive phenomena of nanoparticles-based flocculated materials were limited. Segal *et al.* reported a precipitation-redispersion mechanism for complexation of short chain PAA with cerium oxide nanoparticles.²¹ They showed that addition of PAA to a cerium oxide sols leads to macroscopic precipitation and the solution redispersed into a clear solution of single particles with an anionic PAA corona as the pH increased. In the present report, we found a different precipitation-redispersion behavior for the complexes of the imidazolium cations-modified gold nanoparticles with PAA.

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EXPERIMENTAL

Measurements

^1H NMR spectra were obtained with a JOEL EX-400 spectrometer (400 MHz). UV-visible spectra were measured on a JASCO V-530 spectrophotometer using quartz cuvettes with a 1 cm optical path length. Transmission electron microscopy (TEM) was performed using a JOEL JEM-100SX operated at 100 kV electron beam accelerating voltage. One drop of the solution of the sample was deposited onto a copper grid and the excess of the dropped solution was blotted off the grid with a filter paper, and then the sample was dried under ambient conditions. Thermogravimetric analysis (TGA) was performed using a TG/DTA6200, SEIKO Instruments, Inc. with the heating rate of $10^\circ\text{C min}^{-1}$ up to 900°C under air. FT-IR spectra were recorded on a Perkin Elmer 1600 infrared spectrophotometer using a KBr disk dispersed with the powder sample. Dynamic light scattering (DLS) was measured on a FPAR-1000, Otsuka Electronics Co., Ltd. pH measurements were performed using a pH meter D-21, HORIBA, Ltd.

Materials

Poly(acrylic acid)s ($M_w = 5000, 25000, \text{ and } 250000 \text{ g mol}^{-1}$) were purchased from Wako Pure Chemical Industries, Ltd. Poly(acrylic acid) ($M_w = 2000 \text{ g mol}^{-1}$) was purchased from Aldrich Chemical Co. Poly(styrenesulfonic acid) ($M_w = 70000 \text{ g mol}^{-1}$) was purchased from Polyscience. The other reagents and solvents were used as supplied, unless stated otherwise.

Imidazolium Cations-Modified Gold Nanoparticles (MImCl-AuNP). A procedure was described in our previous paper.⁶ The average diameter of the gold nanoparticles was $4.8 \pm 0.6 \text{ nm}$ as measured by a TEM image by averaging the size of 100 particles. This was well in accordance with a dynamic light scattering (DLS) result ($5.2 \pm 0.8 \text{ nm}$) of MImCl-AuNP in aqueous solution. The organic content of MImCl-AuNP was 17.2 wt % from a thermogravimetric analysis (TGA). The number of the imidazolium cations adsorbed on the surface of the each gold nanoparticle was calculated as 610 based on the fact that the average particle size is 4.8 nm.

Addition of PAA to Aqueous Solution of MImCl-AuNP

A typical procedure is described as follows. In a 20 mL sample bottle, the aqueous solution (5 mL) of MImCl-AuNP (0.5 mg, containing $3.7 \times 10^{-4} \text{ mmol}$ of the imidazolium units calculated from the TGA result) was prepared. To this solution, an aqueous solution (5 mL) of PAA ($M_w = 25000$) (200 mg, 2.8 mmol

of a repeating unit) was added with vigorously stirring. For studying the pH effect on the precipitates, the suspension was acidified with 1.0 M HCl and neutralized with 1.0 M NaOH.

RESULTS AND DISCUSSION

When 200 mg of PAA ($M_w = 25000$) was added to an aqueous solution of MImCl-AuNP (0.5 mg), a red color of the solution gradually disappeared. After stirring for 6 h, a precipitate was observed with a clear colorless supernatant. The colorless supernatant indicates that all the gold nanoparticles were comprised in the precipitate. The pH of the solution was 2.4. After washing the precipitate several times by an acidic aqueous solution adjusted to pH 2.4 by HCl to remove extra PAA, we performed TGA and FT-IR measurements of the precipitate. TGA results showed that the organic components in the gold nanoparticles and the precipitates were 17.2 wt % and 28.9 wt %, respectively. The FT-IR measurement showed the peaks of C=O stretching vibration derived from the carboxylic acid units (1698 cm^{-1}) and the carboxylate anion units (1551 cm^{-1}) in addition to the peak at 1636 cm^{-1} derived from the C=C stretching vibration of the imidazolium cations (Figure 1). The presence of the carboxylate anion in the precipitates after washing by the acidic aqueous solution adjusted to pH 2.4 indicates that the counter anion of the imidazolium cation was exchanged from chloride to the carboxylate anion of PAA. The molar ratio of the carboxylate unit to the imidazolium cation in the precipitate was calculated as 3.1 from the TGA results. From these observations, the precipitate was formed by the electrostatic interaction between MImCl-AuNP and PAA. Addition of glutaric acid (equal mol of a carboxylic unit to that in the case of PAA) instead of PAA ($M_w = 25000$) to the aqueous solution of MImCl-AuNP caused no precipitate.

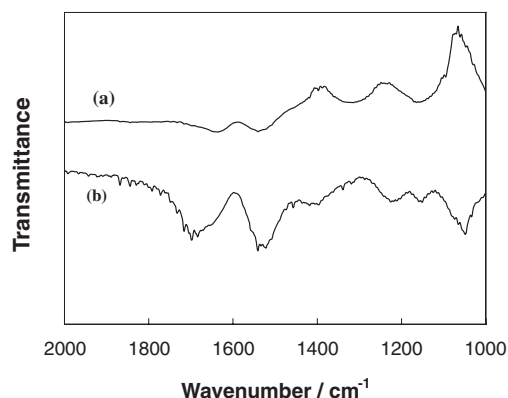


Figure 1. FT-IR spectra of MImCl-AuNP (a) and the precipitates after mixing MImCl-AuNP and PAA ($M_w = 25000$) (b).

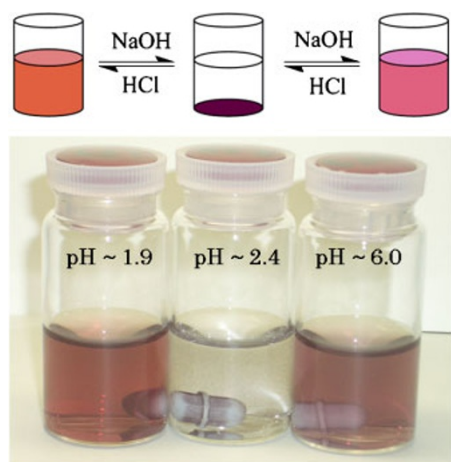


Figure 2. Photograph of various pH solutions of MImCl-AuNP with PAA ($M_w = 25000$).

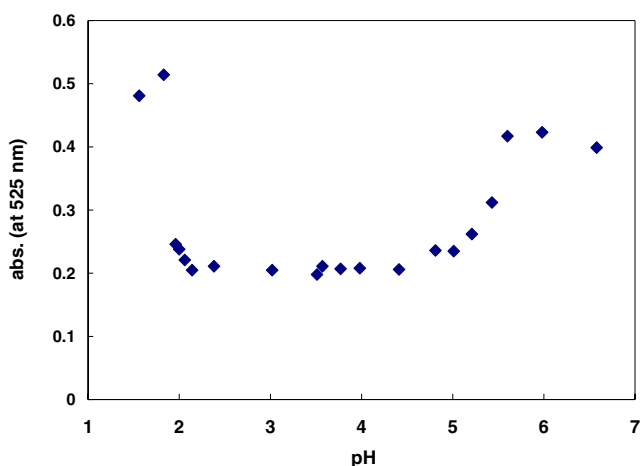


Figure 3. UV-vis absorption intensity at 525 nm of aqueous solution of MImCl-AuNP with PAA ($M_w = 25000$) at various pH.

The resulting precipitate after MImCl-AuNP was mixed with PAA ($M_w = 25000$) in aqueous solution as described above was dissolved into a clear red colored solution when the pH dropped below 1.9 by addition of 1.0 M HCl. Addition of 1.0 M NaOH to the acidified solution caused a precipitate again at the pH of 2.2, and the precipitate was redissolved when the pH rose above 5.5 (Figure 2). Addition of 1.0 M HCl to the final solution reproduced the precipitation-redispersion process until the pH dropped below 1.9. Figure 3 shows the plot of the UV-vis absorption intensity at 525 nm of the aqueous solution of MImCl-AuNP with PAA ($M_w = 25000$) against the pH. The UV-vis absorption maxima of the surface plasmon absorption of MImCl-AuNP at the pH of 6.0 and 1.7 were 528 and 516 nm, respectively (Figure 4). The absorption maximum of the solution at pH 6.0 was red-shifted compared with that in the case of the solution at pH 1.7 and the pristine solution of MImCl-AuNP without PAA ($\lambda_{\max} = 514$ nm). The red shift can be

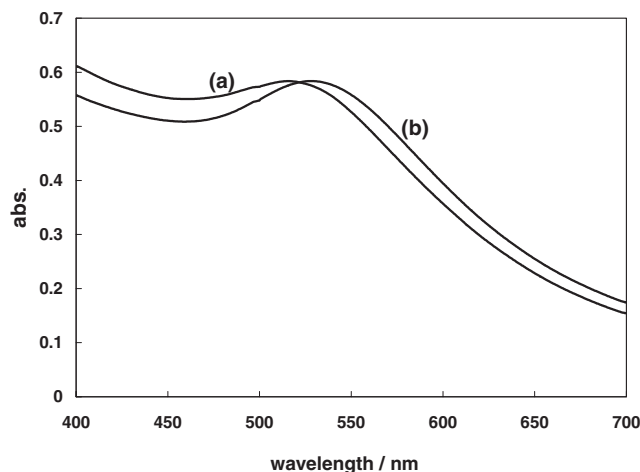


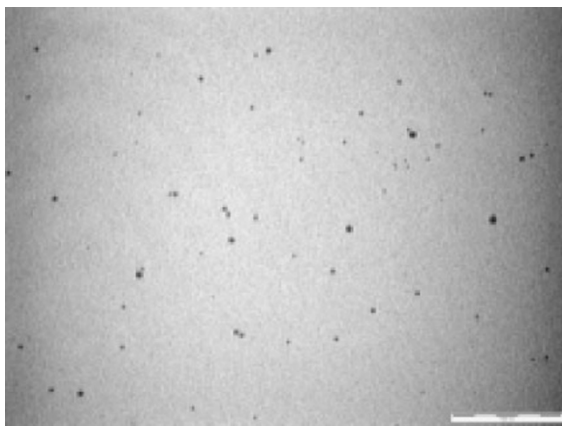
Figure 4. UV-vis absorption spectra of the solutions of MImCl-AuNP with PAA ($M_w = 25000$) (a) at pH 1.5 and (b) at pH 6.0.

attributed to the coupled plasmon absorbance of the gold nanoparticles in closer contact,³ which indicates a formation of particle aggregates in the aqueous solution at pH 6.0. The addition of NaCl (4 mmol) to the aqueous solution of MImCl-AuNP in the presence of PAA at pH 6.0 gave no change of the surface plasmon absorption. The aggregate formation was supported by a TEM observation and a DLS measurement. The TEM image of MImCl-AuNP in the presence of PAA at pH 1.7 indicates the dispersed state of the gold nanoparticles as well as before the addition of PAA (Figure 5a). The TEM image of the sample at pH 6.0 shows the aggregates of the gold nanoparticles and the size of the aggregates was ranging from 40 nm to 150 nm (Figure 5b). A DLS measurement suggested the formation of the aggregates in aqueous solution with a diameter of 115 ± 21 nm.

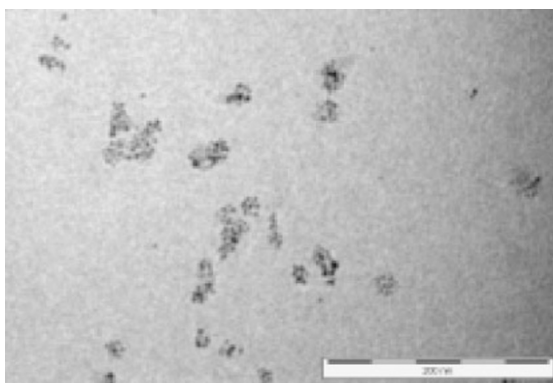
Decrease the addition amount of PAA ($M_w = 25000$) to 100 mg (1.4 mmol of the repeating unit) showed the same phenomenon observed as described above. However, further reduced the amount of PAA ($M_w = 25000$) to 50 mg (0.7 mmol of the repeating unit), no precipitate formed even after 36 h incubation. Although no precipitate was formed, the UV-vis absorption spectrum of the solution shows the surface plasmon absorption at 525 nm, which indicates an aggregate formation.

We studied the effect of the molecular weight of PAA. When 200 mg of PAA ($M_w = 5000$) was added to the solution of the gold nanoparticles, a precipitate was observed after stirring for only 10 min, which was significantly faster than the case of the addition of PAA ($M_w = 25000$) as described above. Precipitate formation was observed less than 1 min after addition of 200 mg of PAA ($M_w = 2000$). In contrast, the addition of 200 mg of PAA ($M_w = 250000$) caused no pre-

(a)



(b)



(c)

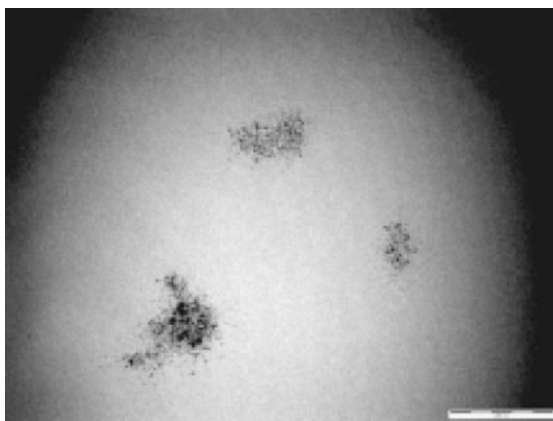


Figure 5. TEM images of MImCl-AuNP with PAA ($M_w = 25000$) (a) at pH 1.5 (scale bar: 100 nm) and (b, c) at pH 6.0 (scale bars: 200 nm).

precipitation even after 2 months. A DLS measurement of this solution, however, indicated the formation of the aggregates with a diameter of 174 ± 29 nm. The TGA results of the obtained precipitates after the addition of the various molecular weights of PAA and washing by the acidic aqueous solution suggest that the organic contents of the obtained precipitates were independent of the molecular weights of PAA (Table I). The molar ratios of the carboxylate unit to

Table I. Results of the precipitates of the gold nanoparticles after addition of PAA

M_w of PAA (g mol^{-1})	Observed precipitation time	Weight loss ^a (wt %)	Number of PAA chain per AuNP ^b
2000	1 min	28.7	5.3
5000	10 min	30.8	33
25000	6 h	28.9	67
250000	no	—	—

^aTGA results of the obtained precipitates after addition of various molecular weights of PAA. ^bThe calculated number of PAA chain per one gold nanoparticle in the precipitates.

the imidazolium cation in the precipitates were calculated as 3.1 to 3.7. If all the imidazolium cations interacted with the carboxylate anions, approximately 70 mol % of the carboxylate units of PAA might be not interacting with the gold nanoparticles. Table I also shows the calculated numbers of the polymer chains tangling per gold nanoparticle in the precipitates. In the case of PAA ($M_w = 25000$), 5 polymer chains tangled per gold nanoparticle. In the case of PAA ($M_w = 2000$), 67 polymer chains tangled per gold nanoparticle. Longer chain PAA has a longer non-interacted chain with the gold nanoparticle than that of shorter chain PAA. Existence of the longer non-interacted chains on the nanoparticles promotes the solubility of the nanoparticles. The behavior of the pH-response of the precipitate after the addition of PAA ($M_w = 5000$) was similar to that after the addition of PAA ($M_w = 25000$). The precipitate after the addition of PAA ($M_w = 2000$) was un-redissolved even after addition of 1.0 M NaOH. We assumed that this difference also derives from the short chain PAA ($M_w = 2000$). In the case of PAA ($M_w = 2000$), the short non-interacted carboxylate units might diminish the electrostatic repulsion for the redissolution.

The proposed mechanism for the pH-responsive phenomena is as follows (Figure 6). After addition of PAA to the aqueous solution of MImCl-AuNP, the counter anion of the imidazolium cation was exchanged from chloride to the carboxylate anion of PAA and interpolymer hydrogen-bondings of the remaining carboxylic acids formed the precipitate. When the pH of the solution dropped below 1.9 by addition of HCl, the protonation of the carboxylate units of PAA in the precipitates promotes the anion exchange of the imidazolium cations to chloride. Thus, the gold nanoparticles redispersed independently of the presence of PAA as before the addition of PAA. When the pH rose above 5.5 by addition of NaOH, the polymer backbones are electrostatically repulsive each other. It was well known that conformation of the anionic polymer, such as PAA, dramatically depending on pH in an aqueous solution.^{22–24} As a result,

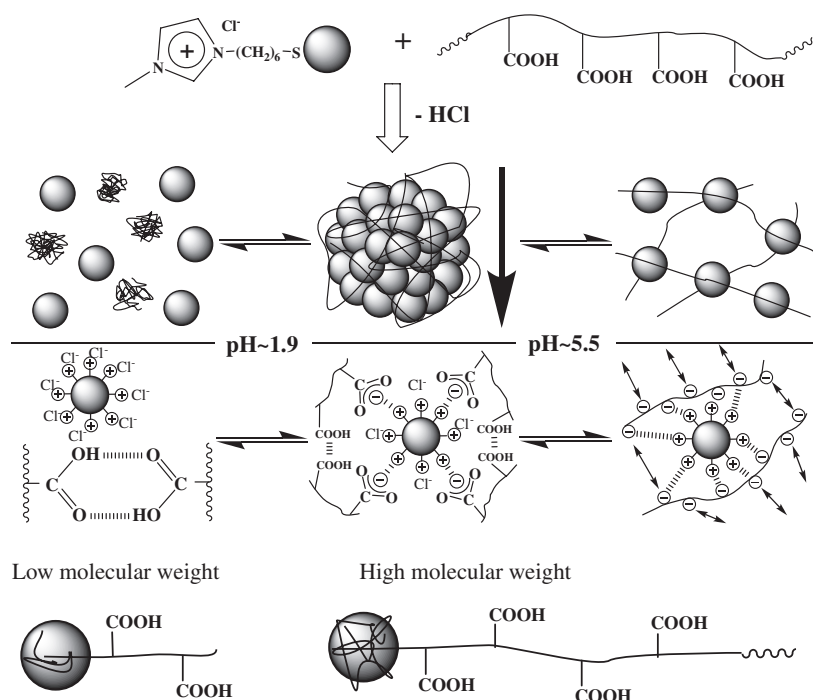


Figure 6. Proposed mechanism of the flocculation and the pH responsive aggregation of MImCl-AuNP with PAA.

although the electrostatic interaction between the imidazolium cations and the carboxylate anions exists as ever, the gold nanoparticles ensure enough dispersions for redissolution, and become redissolved in keeping certain degrees of aggregates. A strong acid containing polymer may not show the pH responsive precipitation-redispersion phenomena. No precipitate was observed after addition of poly(styrenesulfonic acid) (PSSA, $M_w = 70000$) when an equal molar ratio of PSSA to the imidazolium cation as the case of PAA. A DLS measurement of the sample suggested the aggregated state with a diameter range of 60 to 80 nm and the size was nearly unchanged against various pH due to the strong acidity of PSSA.

CONCLUSIONS

We have demonstrated the pH-responsive control of the colloidal dispersions of the gold nanoparticles by using the electrostatic interaction between the cationic gold nanoparticles and PAA. After the addition of PAA, the gold nanoparticles were precipitated by the electrostatic interaction between the imidazolium cations on the surface of the gold nanoparticles and the carboxylate anions of PAA. The precipitates were redissolved and well redispersed when the pH dropped below 1.9 and redissolved with forming aggregates when the pH rose above 5.5. The present study demonstrated that the nanoparticle-based flocculate materials can be applied for pH-responsive control of the colloidal dispersions of gold nanoparticles.

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We dedicate this article to the memory of the Late Emeritus Professor Yoshihiko Ito.

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