Simple and Environmentally Compatible One-pot Synthesis of Au Nanoparticles from Bulk: Separation of Au, Ag, and Cu in Water

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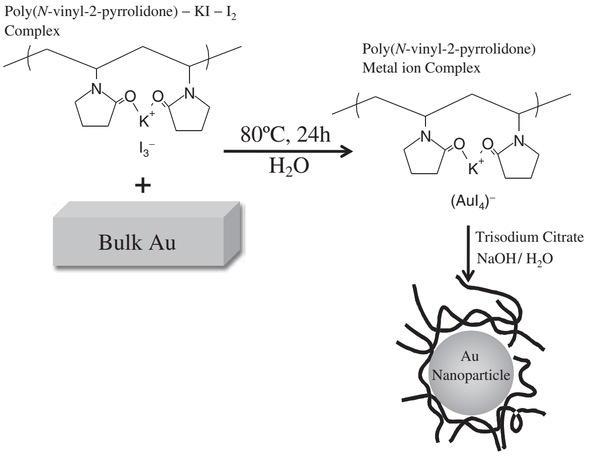
Simple and environmentally compatible one-pot synthesis of Au nanoparticles, starting from dissolving bulk Au into mixed aqueous solution of poly(*N*-vinyl-2-pyrrolidone), potassium iodide, and iodine and ending by isolating Au nanoparticles produced by reducing the dissolved Au ions with sodium citrate, was developed to provide a novel method to separate Au from mixtures of Au, Ag, and Cu.

Au nanoparticles have received much attention from the viewpoint of novel properties such as catalyses[1] and optics[2] because they have quite different properties from bulk Au. On the other hand, bulk Au is known to be chemically stable and have excellent electroconductivity. Thus, the noble metal elements of not only Au but also Ag, Cu, Pd, and Pt have been used for various applications, for example, mobile phones, personal computers, and automobile catalysts. Simple and environmentally compatible methods for recovery of noble metals from used electronic equipment are expected to be developed.[3] However, much energy and special reagents are required such as strong acid or base to collect or recover noble metal elements because of their chemical stability. Previously, Nakao reported a method to dissolve noble metal elements into a halogen–halide–organic solvent system.[4–7] This method does not use strong acid, for example aqua regia, but requires the use of an organic solvent like acetonitrile or methanol. In the present study, we would like to report a selective one-pot synthetic method of Au nanoparticles from bulk by dissolving it into an aqueous solution of poly(*N*-vinyl-2-pyrrolidone) (PVP), potassium iodide, and iodine. This method has several advantages with respect to environmental load because the solvent is only water, no aqua regia is used, and the separation is carried out by ultrafiltration. It is very useful that Au nanoparticles can be obtained directly from discarded electronic products.

The schematic chart of synthesis of Au nanoparticles is shown in Scheme 1. PVP (K30, average molecular weight 40000, 630 mg, 5.6 mmol in monomer unit) was put into a 200-mL two-neck flask with deionized water (70 mL), and the mixtures were stirred at room temperature for 10 min. Potassium iodide (93 mg, 0.56 mmol) was added to the mixtures. After 10 min stirring, iodine (70 mg, 0.28 mmol) was added to the mixtures under stirring. After further 10 min stirring, a noble metal wire (Au, Ag, Cu, Pd, or Pt, $\phi = 0.2$ mm, 0.05 mmol) was added, and the mixtures were heated at 80 °C in an oil bath with a reflux condenser and heated for 24 h. Then, trisodium citrate (200 mg, 0.78 mmol) dissolved in deionized water (20 mL) was added to the reaction mixtures, which were stirred for 10 min. Finally 0.1 mmol L^{-1} sodium hydroxide (10 mL, 1.0 mmol) was added to the mixtures, which were stirred for 20 min.



Scheme 1. The Schematic chart of synthesis of Au nanoparticles from bulk by dissolving with poly(*N*-vinyl-2-pyrrolidone)–KI–I$_2$ in water.

The extent of dissolved metals in solution was determined by measuring weight of wire after the reaction. Within 24 h 100 wt % of Cu and 96.3 wt % of Au were dissolved, but Ag was not. In the case of Ag wire, a weight increase was observed which suggested AgI film formation on the surface of Ag wire and the protection of Ag from oxidation. Only 7.6 wt % of Pd and 1.6 wt % of Pt wires were dissolved in the aqueous solution. These results suggest that noble metal elements could be dissolved selectively by reaction rate.

Figure 1 shows UV–vis absorption spectra of reaction solutions dissolving PVP, KI, and I$_2$. This spectrum shows that the reddish brown reaction solution had an absorption maxima at 290 and 360 nm initially, which could be attributed to I$_3{}^-$ ions produced by the reaction of KI and I$_2$ (eq 1). The curve b in Figure 1 is a spectrum of the solution after 24 h from addition of Au wire. The absorbance at 290 and 360 nm of curve b is lower than that of curve a, implying that I$_3{}^-$ ions were consumed to oxidize Au wire as described by eq 2. K[AuI$_2$] was oxidized to K[AuI$_4$] by I$_3{}^-$ ions again (eq 3). Since the absorbance of [AuI$_4$]$^-$ ions is much weaker than of I$_3{}^-$ ions, the absorption spectrum of [AuI$_4$]$^-$ ions (peaks on 510 and 670 nm[5]) could not be detected.

$$\mathrm{KI} + \mathrm{I_2} \rightarrow \mathrm{KI_3} \qquad (1)$$

$$\mathrm{KI} + 2\mathrm{Au} + \mathrm{KI_3} \rightarrow 2\mathrm{K[AuI_2]} \qquad (2)$$

$$2\mathrm{K[AuI_2]} + 2\mathrm{KI_3} \rightarrow 2\mathrm{K[AuI_4]} + 2\mathrm{KI} \qquad (3)$$

Figure 1c shows the spectrum of the mixed solution after addition of the trisodium citrate solution for reduction of Au ions to produce Au nanoparticles. Representative plasmon resonance

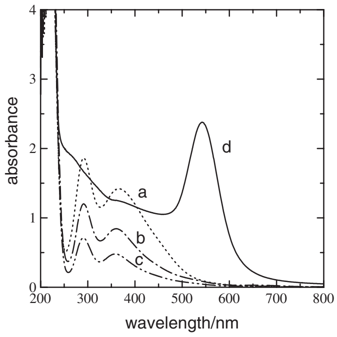


Figure 1. UV–vis absorption spectra of solutions; (a) before oxidation, (b) after oxidation, (c) after addition of citrate, and (d) after reduction. (a), (b), (c) were diluted 50 times.

absorption by Au nanoparticles was not observed, but the absorption peak of I_3^- ions became weak, suggesting that trisodium citrate reduced not only Au^{III} ions but also I_3^- according to eq 4. Here the trisodium citrate was oxidized by I_3^- to produce disodium 1,3-acetonedicarboxylate ($C_5H_4Na_2O_5$).[8] In addition, Au^0 produced by reduction of Au^{III} ions by citrate was reoxidized by I_3^-. In other words, excess I_3^- could prevent Au^{III} ions from being reduced by trisodium citrate. In order to make it possible to reduce Au^{III} ions by trisodium citrate, excess I_2 molecules, which form I_3^- ions by reaction with I^- ions, should be decomposed by addition of NaOH according to eqs 5 and 6. The total reaction is written as eq 7. When a NaOH solution was added to the reaction mixture, the reddish color due to I_3^- disappeared within a few minutes resulting in a transparent pale yellow solution, and then reddish color appeared gradually due to the formation of Au nanoparticle dispersion. Spectrum d had an absorption peak at 540 nm, which was the same position as plasmon resonance absorption of Au nanoparticles.[9] Without NaOH, preparation of Au nanoparticles was not successful even if the reaction solution was heated and stirred for a long time.

$$I_2 + C_6H_5Na_3O_7 \rightarrow C_5H_4Na_2O_5 + HI + NaI + CO_2 \quad (4)$$

$$I_2 + 2NaOH \rightarrow NaIO + NaI + H_2O \quad (5)$$

$$3NaIO \rightarrow NaIO_3 + 2NaI \quad (6)$$

$$3I_2 + 6NaOH \rightarrow NaIO_3 + 5NaI + 3H_2O \quad (7)$$

Figure 2 shows the TEM image and size distribution histogram of Au nanoparticles. The average diameter of nanoparticles is 46.4 nm. The dispersion of nanoparticles was very stable for a few months even without filtration to remove ions, suggesting that nanoparticles were protected strongly by PVP.

Au nanoparticles could be washed by ultrafiltration by a membrane filter of cutoff molecular weight 10000, which supports the strong protection of Au nanoparticles by PVP. If Au nanoparticles could not be protected by PVP, they were aggregated on the membrane filter and could not be recovered from the filter.

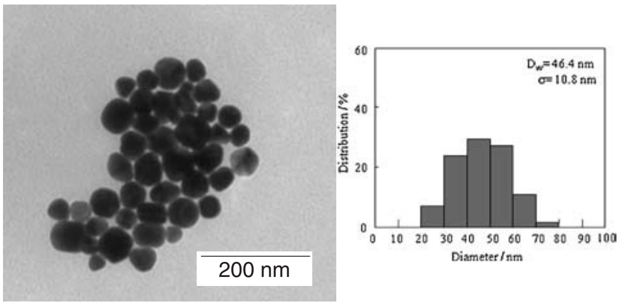


Figure 2. TEM image and size distribution histogram of Au nanoparticles.

In the case of Cu, the Cu wire was dissolved by a similar method, but Cu nanoparticles could not be produced because the reduction of Cu^{II} ions is very difficult by trisodium citrate and because Cu nanoparticles are very easily oxidized by air. Thus, the present method can be applied to separation of Au, Ag, and Cu. Since Ag could not react with the aqueous solution, Ag could be separated from Au and Cu. After the reaction, produced Au nanoparticles can be recovered by filtration, and Cu ions can be recovered in a filtrate solution. In fact, this method was applied to separate Cu and Au. The mixtures of Cu and Au wires were dissolved completely into the aqueous solution in 24 h. After the one-pot reaction, the filtrate separated from the nanoparticles by ultrafiltration was found to contain 66 wt % of charged amount of Cu and 0.3 wt % of charged amount of Au, suggesting that most of Au was recovered as Au nanoparticles and that two third of Cu was as Cu ions in an aqueous solution.

In conclusion, we have presented a selective one-pot synthetic method of noble metals, especially Au nanoparticles from bulk by dissolving them into an aqueous solution of poly(*N*-vinyl-2-pyrrolidone), potassium iodide, and iodine. This method has a lot of advantages in a simple and environmentally compatible process with low cost, because the aqueous solution of PVP, KI, and I_2 is a very popular disinfectant known as povidone–iodine. In addition this provides an environmentally compatible method to separate Au, Ag, and Cu bulk mixture.

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