

Synthesis method for well crystallized alloy nanoparticles in aqueous solution under room temperature by controlling the metal complexes condition

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ABSTRACT

To synthesis the “uniform” and “well-crystallized” alloy nanoparticles, relation between the structure of metal complexes in the aqueous solution and reduction mechanism of these alloy nanoparticles were evaluated. Metal complex conditions in an aqueous solution were expected by the calculation using the critical stability constants. Results of the prediction based on calculation clearly demonstrated that only the $[Pd^{2+}(EDTA)]$ complex was generated independently in the solution with the pH range of 5 to 10. Therefore, conditions of complexes in solution (pH8) were evaluated by Electro Spray Ionization Time of Flight Mass Spectroscopy (ESI-TOF-MS) and also Extended X-ray Absorption Fine Structure (EXAFS). Former results clearly demonstrated that mass number and distribution of detected peaks were almost the same to that of simulated peaks of $[Pd^{2+}(EDTA)]$ derivatives which generated by the ESI methods. EXAFS results also showed that 1st neighbor of Pd was Nitrogen or Oxygen and 2nd neighbor was carbon, thus EDTA attached to Pd. These results indicated that formation of one specific metal complex in the solution was achieved by obeying to the calculation. By the reduction of these controlled mixed solution, only $Pd_{20}Te_7$ was successfully synthesized, since the formations of metal complexes are restricted to $[Pd^{2+}(EDTA)]$ and $[Te^{4+}(\text{citric acid})]$, respectively.

Keywords: well-crystallized alloy nanoparticles, uniform, complex condition, ESI-TOF-MS

1 INTRODUCTION

Many attempts to prepare the alloy and metallic nanoparticles by various methods have been reported [1]. However, in spite of the objective to obtain alloy materials, the as-prepared metallic nanoparticles often exhibited inhomogeneous compositions and multi-crystalline structures [2,3], which does not adequate for the industrial applications, such as catalysts and electronic devices. Depending on the synthesis conditions, alloy catalysts with various structures and compositions can be prepared. As a consequence, undesirable by-products may co-exist, or the entire catalytic activity may be reduced through catalytic reactions due to the formation of compounds with various surface structures and compositions other than those of

objective alloy[4]. Thus, the synthesis method for “uniform” and “well-crystallized” alloy nanoparticles should be developed.

Metallic nanoparticles are well known to be easily synthesized in the liquid phase by the reduction of metal ions and/or complexes by many traditional methods. In this system, various metal salts and metal complexes are formed simultaneously and their consequent reduction gives rise to a mixture of various kinds of particles, such as single metal, alloy nanoparticles, etc. [5]. In other words, the concomitance of various ions and/or complexes in the starting solution leads to uncontrolled reduction, consequently followed by the formation of undesired mixtures of metal particles caused by the differences in reduction rates of different metal complexes that originated from different precursory metal species that existed in the solution. Finally, the as-prepared alloy nanoparticles have various crystal phases and/or inhomogeneous structures. Thus, in order to synthesize uniform and well-crystallized alloy nanoparticles, the reduction rates of metal species in the starting solution should be made equal.

So, we tried to control the aqueous solution conditions to restricting to the formation of one specific metal complex by utilizing the calculation method [6]. As a result, uniform and well-crystallized $Pd_{20}Te_7$ alloy nanoparticles were successfully synthesized from aqueous solution under room temperature [6]. These results indicate that this method has the possibility to produce various alloy nanoparticles at these economical and environmental friendly conditions. To do so, synthesis mechanism should be investigated.

Therefore, in this study, relation between the structure of metal complexes in the aqueous solution and reduction mechanism of these alloy nanoparticles were evaluated. Pd-Te alloy catalysts were selected to the target materials.

2 EXPERIMENTAL

The concentrations of Pd complexes at various pH values of the aqueous solution were calculated by using the critical stability constants and obeying to the ref.6

Catalysts were prepared by obeying to the following procedure. Sodium tetrachloropalladate (II) (Na_2PdCl_4 , Soekawa Chemical, Japan) and tellurium (IV) chloride ($TeCl_4$, Soekawa Chemical, Japan) were used as Pd and Te sources, respectively. EDTA and citric acid were used as

complex reagents for Pd and Te, respectively. By obeying to the ref.6, concentration of these was adjusted as follows. (A) Pd solution: 0.004mol/l Na_2PdCl_4 and 0.008mol/l EDTA, (B) Te solution: 0.0014mol/l TeCl_4 and 0.0056mol/l citric acid, and (C) Pd+Te solution: 0.004mol/l Na_2PdCl_4 , 0.008mol/l EDTA, 0.0014mol/l TeCl_4 , and 0.0056mol/l citric acid. The pH of these solution was adjusted to (I)5, (II) 10 and (III)13 by using HNO_3 and/or NaOH solutions. As necessary, hydrazine solution, which adjusted to the same pH with metal complex solutions, were added. Final volume was 50ml constant in each case.

These solution were evaluated by using the electro spray ionization time of flight mass spectroscopy method (Bruker Co.,Ltd, micrOTOF II system, denoted as ESI-TOF-MS) and cyclic voltammetry (CAMRY Instruments Co.,Ltd, Reference 600 Potentiostat/Galvanostat/ZRA system, denoted as CV). The Cyclic voltammograms were measured by using a glassy carbon electrode as the working electrode at a scan rate 10 mV/s, room temperature and were first scanned from Open circuit potential (OCP) to the negative direction between -1.3 to $+1.3$ V. CVs were repeated four cycles between -1.3 to $+1.3$ V.

The structure and morphology of washed and dried products were analyzed by using XRD (Rigaku Co.,Ltd., Rad-C system, $\text{CuK}\alpha$, 40KV, 30mA) and HR-TEM/EDX (Hitachi Co.,Ltd, HF-2000 Field Emission TEM).

3 RESULTS AND DISCUSSION

Figure 1 shows the results of the calculation in the cases of (a) dissolution of Na_2PdCl_4 into distilled water and (b) addition of H_4EDTA as a complexing reagent to (a). In the case of (a), various Pd- Cl_x complexes ($X=2-4$) are formed in the acid condition ($\text{pH}<7$), while $[\text{Pd}^{2+}(\text{OH})_2]$ is predominant in basic condition. On the other hand, in the cases of (b), $[\text{Pd}^{2+}(\text{EDTA})]$ are expected to preferred in the pH range between 4 and 10. Here, the solubility of $[\text{Pd}^{2+}(\text{OH})_2]$ are relatively low. Thus, from the above results, it can be expected that a uniform solution condition can be achieved only when using EDTA in the pH range between 4 and 10.

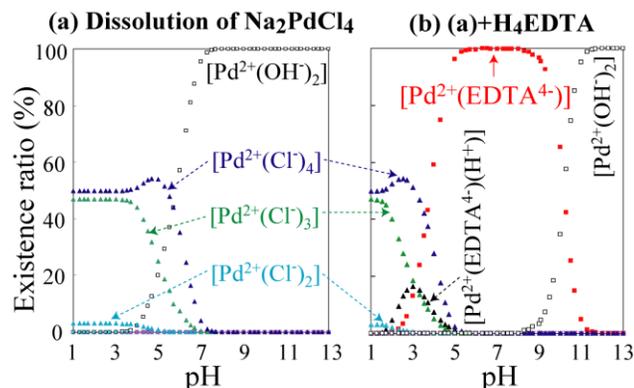


Fig. 1 Results of the calculation of (a) dissolution of Na_2PdCl_4 and (b) H_4EDTA addition to (a).

Therefore, conditions of complexes in solution were evaluated by Electro Spray Ionization Time of Flight Mass Spectroscopy (ESI-TOF-MS). Figure 2 shows the ESI-TOF-MS spectra of $\text{Na}_2\text{PdCl}_4\text{-H}_4\text{EDTA}$ solution at pH8. Negative ions were detected (measurement mode : negative mode). As shown in figure, it become apparent that peak profile can be classified into two, one is simple peaks and other is peaks with wide distribution. Former group is considered to originate from addition or dissociation species of EDTA. For example, the peak at $m/z=335.04$ and 715.06 is considered to attribute for $[(\text{EDTA}^{4-})(\text{H}^+)](\text{Na}^+)_2$ and $[(\text{EDTA}^{4-})_2(\text{H}^+)](\text{Na}^+)_6$, respectively. On the other hand, later group can be classified into four (A-D) group as shown in the figure.

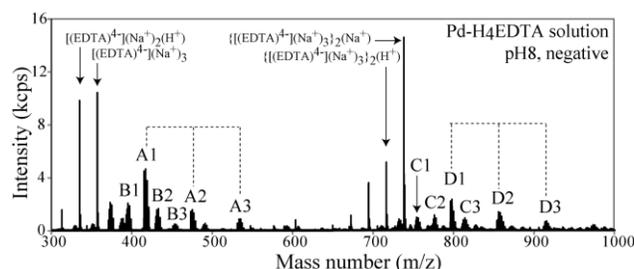


Fig.2 Result of ESI-TOF-MS analysis of $\text{Na}_2\text{PdCl}_4\text{-H}_4\text{EDTA}$ solution at pH8

Figure 3 shows the measured ESI-TOF-MS spectrum at A1 position in Fig.2 and simulated spectrum of $[(\text{Pd}^{2+})(\text{EDTA}^{4-})](\text{Na}^+) + [(\text{EDTA}^{4-})](\text{Na}^+)_4(\text{Cl})$ species. In the case of measured spectrum at A1 position, the peaks are distributed at $m/z=414.98, 415.95, 416.96, 417.96, 418.95$ and 420.95 . The relative peak intensities are 97, 72, 100, 13, 81 and 38 (intensity of most strong one at $m/z=416.96$ was denoted to 100). On the other hand, from the simulated spectrum, the peaks are distributed at $m/z=414.98, 415.95, 416.95, 417.96, 418.95$ and 420.95 , and relative peak intensities are 92, 74, 100, 13, 83 and 38. Here, relative peak intensities are originated from natural abundance of element. Thus, positions and also the natural abundance ratio of the peaks at A1 position is almost the same to $[(\text{Pd}^{2+})(\text{EDTA}^{4-})](\text{Na}^+) + [(\text{EDTA}^{4-})](\text{Na}^+)_4(\text{Cl})$. Taking the mass number of $[(\text{EDTA}^{4-})](\text{Na}^+)_4(\text{Cl})$ is $m/z=414.98$ and this species shows the simple peak (as already mentioned in Fig.2) into consideration, it can be said that main species of measured spectrum at A1 position was $[(\text{Pd}^{2+})(\text{EDTA}^{4-})](\text{Na}^+)$. Because of the ionization method, it can be considered that Na^+ was added to $[(\text{Pd}^{2+})(\text{EDTA}^{4-})]$. The interval between to A2-A1 and A3-A2 is 57.967 and 57.953, respectively, and this value was consistent with the mass number of NaCl (here we notice that this value is not coincident to the simple sum of average mass number of Na (22.98977) and Cl (35.453)). Thus, it can be said that measured species at A2 and A3 position are $[(\text{Pd}^{2+})(\text{EDTA}^{4-})](\text{Na}^+)_2(\text{Cl})$ and $[(\text{Pd}^{2+})(\text{EDTA}^{4-})](\text{Na}^+)_3(\text{Cl})_2$, respectively. In the same manner, it can be said that measured species at B1, C1 and D1 position are $[(\text{Pd}^{2+})(\text{EDTA}^{4-})](\text{H}^+)$ (maximum peak position : $m/z=394.97$), $[(\text{Pd}^{2+})(\text{EDTA}^{4-})]$

)₂[(H⁺)₂(Na⁺)₃ (m/z=753.00) and [(Pd²⁺)(EDTA⁴⁻)₂](Na⁺)₅ (m/z=796.97), respectively.

These results clearly indicated that main species in Na₂PdCl₄-H₄EDTA solution at pH8 is [(Pd²⁺)(EDTA⁴⁻)].

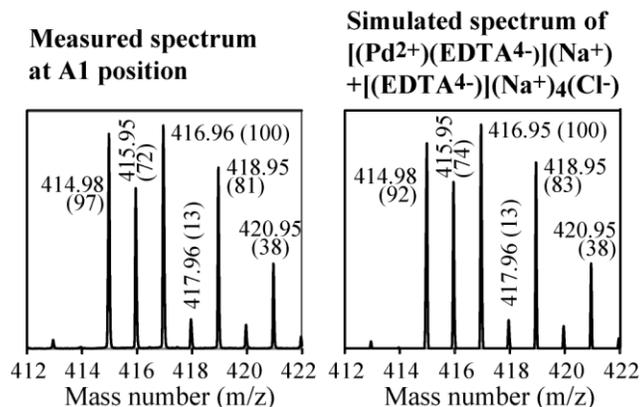


Figure 3 Measured ESI-TOF-MS spectrum at A1 position in Fig.2 and simulated spectrum of [(Pd²⁺)(EDTA⁴⁻)](Na⁺) + [(EDTA⁴⁻)](Na⁺)₄(Cl) species

Figure 4 shows the (A) raw data and (B) Fourier transformed data of Na₂PdCl₄-H₄EDTA solution at pH8, which was already shown in ref.6. These results clearly demonstrate that the 1st nearest neighbors of Pd were oxygen and/or nitrogen, and the 2nd nearest neighbor was carbon in all cases. Moreover, in spite of the addition of TeCl₄, solution and/or citric acid solution, no large change was observed in the EXAFS spectrum. Thus, as same as to the results of ESI-TOF-MS, Pd was preferentially coordinated with EDTA⁴⁻, since many metal ions bind with either oxygen or nitrogen of EDTA to form chelate compounds. On the other hand, the results of EXAFS analysis at Te K-edge (not shown) was indicated that only Te-citric acid complex species was formed in the Na₂PdCl₄-H₄EDTA-TeCl₄-citric acid solution. Thus, it can be concluded that EDTA was preferentially bonded with Pd under the present experimental conditions, in spite of the possibility of EDTA forming a complex with Te.

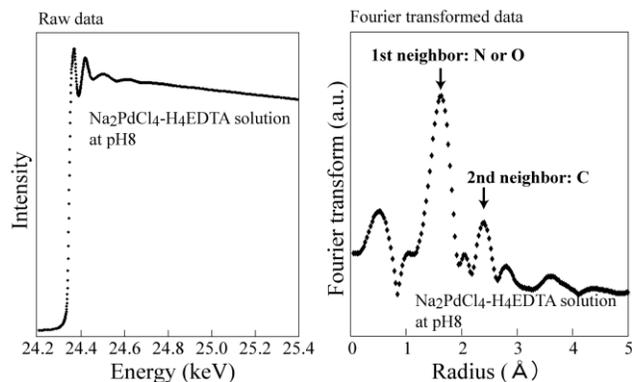


Figure 4 Result of EXAFS analysis of Na₂PdCl₄-H₄EDTA solution at pH8 (Ref. 6)

From the results mentioned above, we can conclude that Pd and/or Te metal complexes were successfully restricted into [Pd²⁺(EDTA⁴⁻)] complex and/or [(Te⁴⁺)(citric acid)] complex, respectively.

Figure 5 shows the XRD profiles of samples formed under different solution pH at 25°C and HR-TEM micrograph of synthesized material. XRD profiles of the products at pH 1-3 showed many diffraction peaks, indicating the presence of various crystals in the product. On the other hand, all diffraction lines of the samples obtained in the pH 5-10, thus Pd and/or Te metal complexes were restricted into [Pd²⁺(EDTA⁴⁻)] complex and/or [(Te⁴⁺)(citric acid)] complex, were clearly assigned only to Pd₂₀Te₇ (PDF# 43-810). By increasing the pH to 12, XRD results indicated that Pd metal (PDF# 46-1043) was predominant, and the presence of Pd₂₀Te₇ was negligible.

These results were in agreement with the results obtained from metal complex calculations in the pH range between 1 and 12. For example, when various Pd-Cl complexes are co-existed (pH 1-3), PdTe alloys with different compositions and crystal structures that were generated as a result of uncontrolled reduction of several complexes coexisted in this pH range, while formation of Pd metal at pH 12 is possible through direct reduction of Pd(OH)₂. On the other hand, the successful synthesis of Pd₂₀Te₇ was possible through precise control of the solution conditions (5 < pH < 10) that facilitated the formation of [Pd²⁺(EDTA)] species and [(Te⁴⁺)(citric acid)] species only. Namely, Pd₂₀Te₇ were predominantly synthesized only in this pH range, because the reduction rates of Pd and also Te complexes were restricted to be the same by precise control of the solution conditions.

HR-TEM micrograph indicated that nanoparticles with highly crystalline and distinct lattice structures are synthesized. HR-TEM/EDX analysis was carried out by focusing the beam on a number of single particles. The atomic percentage of Pd ranged narrowly between 76.0-76.6 % in PdTe bimetallic particles, that is, Pd₂₀Te_{6.1}-Pd₂₀Te_{6.3} and the presence of neither Pd nor Te nanoparticles were detected.

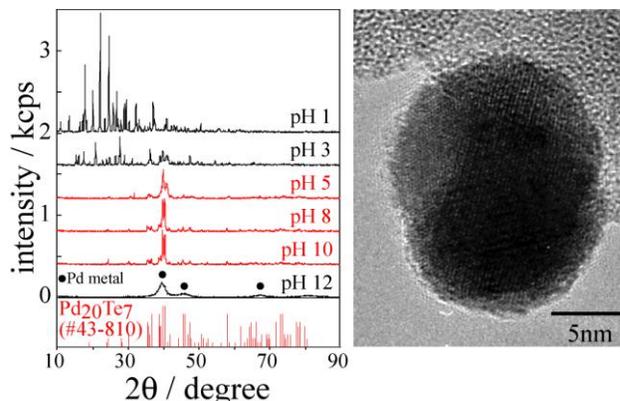


Figure 5 XRD profiles of samples formed under different solution pH at 25°C and HR-TEM micrograph of synthesized material

Since the reduction rate of the Pd-EDTA complex was slightly faster than that of Te-citric acid complex [6], Pd metal nuclei may have formed first during the temperature rise, followed then by the growth of Pd₂₀Te₇ alloy on the Pd nuclei by increasing temperatures.

From CV measurement results, one reduction wave was detected at around -0.89V from Te-citric acid solution, while that was observed at around -1.03V in the case of Na₂PdCl₄-H₄EDTA solution. So, electrodeposition was performed at -1.00V and at -1.10V in the case of former and later solution, respectively. As a result, Te metal (#36-1452) and Pd metal (#46-1043) were electrodeposited from each solution. Thus, these results shows that [(Te⁴⁺)(citric acid)] and [Pd²⁺(EDTA)] complex were reduced into Te metal at -0.89V from Te-citric acid solution and Pd metal at -1.03V from Na₂PdCl₄-H₄EDTA solution, respectively.

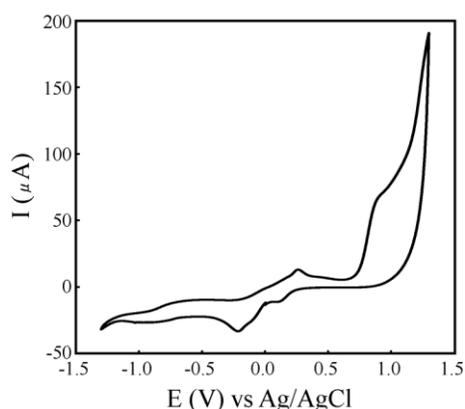


Figure 6 CV result of the solution containing Na₂PdCl₄-H₄EDTA-Te-citric acid, dissolved in 0.1MKCl solution

Figure 6 shows a CV result of the solution containing Na₂PdCl₄-H₄EDTA-Te-citric acid, dissolved in 0.1MKCl solution. As shown in figure, reduction waves were observed at the peak potential of -0.19V and 0.16V, while oxidation waves were detected at around 0.21V and 0.89V. XRD result of materials electrodeposited at -0.30V from Na₂PdCl₄-H₄EDTA-Te-citric acid solution shows that Pd-Te alloy (Pd₂Te, PDF#11-0450) was synthesized. This result means that Pd and Te complex can be reduced to Pd-Te alloy at -0.30V in the solution. On the other hand, open circuit potential (OCP) in mixed solution of Na₂PdCl₄-H₄EDTA-Te-citric acid and reducing agent was -0.28V. OCP is considered to be almost same as mixed potential in this system. Therefore, Pd₂₀Te₇ alloy nanoparticles were synthesized because the mixed potential in the solution was decreased to -0.28V by reducing agent, at which Pd and Te complex can be reduced to Pd-Te alloy. However, it emphasized that reduction potential of Pd-Te mixed condition was apparently differed from that of [(Te⁴⁺)(citric acid)] and/or [Pd²⁺(EDTA)] complex. Thus, it should be considered that Pd₂₀Te₇ alloy was synthesized as the results of the formation of multi metal complex by [Pd²⁺(EDTA)], [(Te⁴⁺)(citric acid)] and hydrazine, or of the induced co-electrodeposition of Te by Pd (or Pd by Te).

4 CONCLUSIONS

In this study, to synthesis the “uniform” and “well-crystallized” alloy nanoparticles, relation between the structure of metal complexes in the aqueous solution and reduction mechanism of these alloy nanoparticles were evaluated.

Results of the prediction based on calculation using critical stability constants clearly demonstrated that only the [Pd²⁺(EDTA)] complex was generated independently in the solution with the pH range of 5 to 10. ESI-TOF-MS results showed that mass number and distribution of detected peaks were almost the same to that of simulated peaks of [Pd²⁺(EDTA)] derivatives. On the other hand, EXAFS results also showed that 1st neighbor of Pd was Nitrogen of Oxygen and 2nd neighbor was carbon, thus EDTA attached to Pd to form [Pd²⁺(EDTA)] species. Thus, it can be said that one specific metal complex, [Pd²⁺(EDTA)] and [Te⁴⁺(citric acid)], was successfully synthesized in the solution. By the reduction of these controlled mixed solution, only the uniform and well-crystallized Pd₂₀Te₇ alloy nanoparticles was successfully synthesized, since the reduction rate was restricted and continuous formation of multi metal complex such as Pd-EDTA-Te-citric acid-hydrazine, or of the induced co-electrodeposition.

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