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Room-Temperature Synthesis of Cobalt Nanoparticles by Electroless Deposition in Aqueous Solution

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Co nanoparticles have great scientific and technological importance due to their unique properties that are different from the bulk. The formation of Co nanoparticles has been extensively studied over the years, leading to a wide variety of synthesis methods, such as thermal decomposition, micellar reduction, sonochemical reduction, and simple chemical (solution) reduction. Most of the methods are conducted in an organic solvent at an elevated temperature. However, the synthesized Co nanoparticles are usually polydispersed and amorphous containing boron.

In this article, we present a method of preparation of Co nanoparticles with diameters of 24–110 nm by electroless deposition (chemical reduction) in an aqueous solution at room temperature. The reduction process is monitored by an in situ measurement of a mixed potential. The mixed potentials are converted to the values against SHE.

Results and Discussion

In the present process, several cathodic and anodic partial reactions occur simultaneously. The main cathodic partial reactions are Pt deposition, Co deposition, and H₂ generation. Because the oxidation–reduction potential of the Pt(IV)/Pt redox pair is more positive than those of Co(II)/Co and H₂O/H₂ redox pairs, Pt(IV) ions from the nucleating agent H₂PtCl₆ are first reduced by hydrazine to form minute Pt nanoparticles. The Co(II) ions are then reduced by hydrazine, and the Co atoms are deposited preferentially on the surface of the Pt nanoparticles, which are the heterogeneous nucleation sites of Co nanoparticles. Co deposition occurs concurrently with the hydrogen generation. The main cathodic partial reactions can be written as

Pt deposition

Pt(IV) + 4e → Pt [1]

Co deposition

Co(II) + 2e → Co [2]

H₂ generation

2H₂O + 2e → H₂ + 2OH⁻ [3]

Anodic partial reactions are primarily hydrazine oxidation reactions

N₂H₄ + 4OH⁻ → N₂ + 4H₂O + 4e [4]

N₂H₄ + OH⁻ → ½N₂ + NH₃ + H₂O + e [5]

Therefore, the overall cobalt deposition reactions can be obtained by combining Reactions 2-5 as follows

Co(II) + 2N₂H₄ + 2OH⁻ → Co + 2N₂ + 2NH₃ + 2H₂O [6]

Co(II) + 2N₂H₂ + 2OH⁻ → Co + N₂ + 2NH₃ + 2H₂O [7]

Figure 1 shows the change in the mixed potentials during the reactions in the aqueous solutions containing different concentrations of nucleating agent, H₂PtCl₆. From the thermodynamical viewpoint, Co can be deposited when the mixed potential is less than the oxidation–reduction potential of the Co(II)/Co redox pair (E°Co(II)/Co) calculated by the Nernst equation and the activity of Co²⁺ aquo ions of about 8.2 × 10⁻¹² in equilibrium with abundant Co(OH)₂ at pH 12. Because the mixed potentials without H₂PtCl₆ are fluctuated, their average values are plotted in Fig. 1a. The instability of the mixed potentials is due to the very small current densities during the
reaction. The average values are obviously much larger than $E_{\text{Co(II)/Co}} = -0.62$ V throughout the reaction. Naturally, no Co nanoparticles are formed even after 2 h.

In contrast, the mixed potentials shift more negatively, and the reduction of Co(II) ions occurs faster with an increase in the concentration of H$_2$PtCl$_6$. In the presence of 0.022 mM H$_2$PtCl$_6$, the mixed potential drops to $E_{\text{Co(II)/Co}}$ about 5 min after the addition of N$_2$H$_4$, and the color of the solution changes to black. When H$_2$PtCl$_6$ is 0.22 mM, the mixed potential is equal to $E_{\text{Co(II)/Co}}$ after about 2 min, and the reduction of Co(II) ions occurs simultaneously. Further increase in the H$_2$PtCl$_6$ concentration results in an instantaneous drop of the mixed potentials below $E_{\text{Co(II)/Co}}$ and a spontaneous change in the color of the solution. Because of the acceleration of the reaction rates with the nucleating agent, it is plausible that the Pt nanoparticles formed from H$_2$PtCl$_6$ act as catalysts for Co(II) reduction, as well as nucleation sites for Co nanoparticles. It has been reported that hydrazine is catalytically oxidized on the surface of Pt nanoparticles. Thus, the reduction of Co(II) ions is accelerated at the surface of the Pt nanoparticles, which are simultaneously the heterogeneous nucleation sites of Co nanoparticles. Small Co nanoparticles are then formed. The decrease in the mixed potential with the increase in the concentration of H$_2$PtCl$_6$ is explained by considering that the mixed potential is mainly controlled by a change in the current density for hydrazine oxidation. The oxidation of hydrazine is generally slow at room temperature. However, the addition of H$_2$PtCl$_6$ accelerates the oxidation reaction due to the catalytic activity of the small Pt nanoparticles. The current density for hydrazine oxidation therefore increases, which reduces the mixed potential. During the precipitation of the Co nanoparticles, significant gas evolution occurs and a large concentration of hydrazine in the solution is depleted. This leads to a gradual increase in the mixed potentials in Fig. 1b-d.

The scanning electron microscope (SEM) images of the Co nanoparticles synthesized by the present method are shown in Fig. 2. The mean particle size of the Co nanoparticles decreases with an increase in the concentration of H$_2$PtCl$_6$, which shows that the nucleating agent apparently works as nuclei of the Co nanoparticles. The smallest Co nanoparticles of 24 nm in diameter are obtained with the addition of 2.2 mM H$_2$PtCl$_6$. The relative standard deviations of the sample size are about 12–16%. Quite narrow size distributions are obtained. The Co nanoparticles are interlinked at random directions, which is due to the magnetic attraction among the nanoparticles.

XRD profiles of the products prepared in the solutions containing various concentrations of the nucleating agent H$_2$PtCl$_6$ are shown in Fig. 3. Without adding the nucleating agent, only the peaks of Co(OH)$_2$, which is the intermediate product during the reaction, are present, as shown in Fig. 3a. Both hexagonal close-packed (hcp) and face-centered cubic (fcc) Co nanoparticles are fabricated in the solutions containing the nucleating agents. These XRD profiles are consistent with the change in the mixed potentials in Fig. 1.

The strongest peak at 68.0° and the peak at 80.5° are due to 111 and 200 fcc Co, respectively. The peak width becomes larger with an increase in the concentration of H$_2$PtCl$_6$. This indicates that the crystallite sizes of the Co nanoparticles decrease in the solution containing the larger H$_2$PtCl$_6$ concentration. This result coincides with the change in the particle morphology by SEM.

The distinct 100 and 101 hcp peaks are also present at 63.8° and 73.6°, respectively. Though the 002 hcp Co peak exists at 68.9°, it is concealed by the large 111 fcc Co peak. Besides, because the maximum hcp Co peak is 101 at 73.6°, the fcc Co phase is dominant in the present Co nanoparticles. This is consistent with the previous study that the major crystalline structure of Co is fcc in the nanoparticles, and this tendency becomes significant in the smaller particles.

In the XRD profiles in Fig. 3c and d, a very diffused peak exists at 55.5°. This peak is ascribed to CoO 111. Thus, the very thin surface layer of Co nanoparticles of smaller sizes, i.e., 24–54 nm in diameter, is oxidized. This CoO is formed during the washing process and the XRD measurements after the reaction.

**Conclusion**

The catalytic property of the nucleating agent H$_2$PtCl$_6$ enables us to prepare metallic Co nanoparticles of 24–110 nm diameter at room temperature by electrolysis deposition (chemical reduction) with hydrazine in aqueous solution. The Co(II) reduction rate and the mean particle size of the Co nanoparticles strongly depend on the concentration of H$_2$PtCl$_6$, which are observed by in situ measurements of
the mixed potential. In the presence of the nucleating agent, the mixed potential quickly drops below the oxidation-reduction potential of the Co(II)/Co redox pair $E_{\text{Co(II)/Co}}$, which leads to the faster Co(II) reduction and the formation of smaller Co nanoparticles. In contrast, without adding nucleating agents, the mixed potential is above $E_{\text{Co(II)/Co}}$, and no Co nanoparticle is prepared.

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References