HOKKAIDO UNIVERSITY

Title	Size-controlled Ni nanoparticles formation by solution glow discharge
Author(s)	Saito, Genki; Hosokai, Sou; Akiyama, Tomohiro; Yoshida, Souki; Yatsu, Shigeo; Watanabe, Seiichi
Citation	Journal of the Physical Society of Japan, 79(8), 083501-1-083501-3 https://doi.org/10.1143/JPSJ.79.083501
Issue Date	2010-07
Doc URL	http://hdl.handle.net/2115/44102
Rights	Copyright (C) 2010 The Physical Society of Japan
Type	article (author version)
File Information	16074.pdf

Instructions for use

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Size-Controlled Ni Nanoparticles Formation by Solution Glow Discharge

Genki SAITO, Sou HOSOKAI, Tomohiro AKIYAMA*, Souki YOSHIDA, Shigeo YATSU, and Seiichi WATANABE

Center for Advanced Research of Energy and Materials, Hokkaido University, Sapporo 060-8628

We report the size control of Ni nanoparticles generated via solution glow discharge and focus on the effect of electrolyte concentration on Ni nanoparticles. In our experiments, voltage was applied to generate a plasma in NaOH electrolytes with concentrations ranging from 1.0 to 0.001 kmol m^{-3}. The applied voltage strongly depended on the electrolyte concentration, and interestingly, product size decreased with electrolyte concentration; for example, (mean diameter, applied voltage, electrolyte concentration) = (148 nm, 90 V, 0.5 kmol m^{-3}), and (70 nm, 590 V, 0.001 kmol m^{-3}). These results suggested the possibility of using plasma electrolysis for synthesizing size-controlled nanoparticles by changing only electrolyte concentration.

KEYWORDS: nanoparticles, electrolyte concentration, voltage, glow discharge, electrolyte concentration, electrode surface, size-controlled

*E-mail: takiyama@eng.hokudai.ac.jp

The synthesis of nanoparticles by various methods, such as laser ablation,[1-4] the use of RF plasma,[5] and flash synthesis,[6,7] has drawn attention worldwide. In particular, glow discharge plasma electrolysis[8] has been newly applied to the synthesis of micro-/nanoparticles in a solution.[9,10] In this method, the surface of the cathode is partially melted as a raw material by the local concentration of current induced by electrothermal instability[11,12] to produce nanoparticles under plasma conditions. Glow discharge plasma electrolysis has many advantages: (1) simple experimental setup, (2) no need to control atmosphere, (3) easy mass production, (4) formation of spherical nanoparticles by partial melting, (5) applicability to any electrically conductive metal/alloy, (6) production of a nonequilibrium phase, (7) generation of hydrogen and oxygen by the electrolysis of water[13], and so on.

Recently, Toriyabe et al.[10] have reported the synthesis of nickel, titanium, silver, and gold nanoparticles via plasma electrolysis, in which voltages of 100–160 V were applied in an alkali solution of K_2CO_3 with a constant concentration of 0.1 kmol m^{-3}. In their experiments, the spherical Ni products became relatively small at the high voltage required for maintaining the plasma, and the smallest products obtained at 160 V had mean diameters approaching 100 nm. These results suggested the possibility of controlling the size of the product by the applied voltage. However, to the best of our knowledge, the relationship between the voltage and the particle size has not yet been reported. Therefore, we studied the production of Ni nanoparticles by plasma electrolysis in a wide range of voltages, in which the relationship between the voltage applied for maintaining the plasma and the size of the product is mainly examined. Uniquely, we used different electrolyte concentrations ranging from 1.0 to 0.001 kmol m^{-3} in order to vary the applied voltage over a wide range, and carried out experiments using the same electric power supply.

Figure 1(a) shows the experimental apparatus used. Electrolysis experiments were performed under stable conditions of power supply (ZX800H, Takasago). A platinum wire (length: 1000 mm, diameter: 0.5 mm, purity: 99.98 mass%; Nilaco) as the anode was bent into a half-round mesh. In contrast, a nickel wire (diameter: 1.0 mm, purity: 99 mass%; Nilaco) as the cathode was covered with an electrically insulated quartz tube to keep the length of the exposed part constant at 10 mm, with this exposed part functioning as the net

actual electrode. The solution temperature at a depth of 10 mm was recorded using a polymer-coated thermistor thermometer (Ondotori TR-71Ui, T&D) every 5 s.

In the experiments, voltage was applied at a rate of 10 V/min until the start of ignition to maximize nanoparticles production, and the current and temperature were recorded during this process. We observed that the plasma emission propagated over the electrode shortly after ignition. Then, the voltage was fixed to a constant value for 1 h; during this period, the electric power W was kept at 40 W. After the experiments, the electrolyte was first passed through a membrane filter with a pore size of 0.45 μm to exclude dust particles[14-16] and it was then dried to recover the final products. The size of the recovered particles was determined using a fiber optic dynamic light-scattering photometer (FDLS-3000, Otsuka Electronics, Co., Ltd.) with a nominal measurable particle size range of 0.5 to 5000 nm. The microstructure and morphology of the products were also investigated by Hitachi H-700 transmission electron microscopy (TEM) at an operating voltage of 200 kV by analyzing a water containing nanoparticles that was dropped on a collodion-coated Cu microgrid. In contrast, the surface of the Ni electrode before/after experiments was observed by JEOL JSM-7400F field-emission scanning electron microscopy (FE-SEM).

Figure 1(b) shows the histories of cell voltages in NaOH electrolytes with different concentrations. When voltage was applied, ignition occurred in all the experiments, except at a electrolyte concentration of 1.0 kmol m^{-3}. Figure 1(c) shows photographs of the electrode during plasma electrolysis; photograph no. 2 shows the start of glow discharge (170 V, breakdown voltage) and photograph nos. 3/4 are obtained before/after ignition (212 V, ignition voltage). The plasma phenomena emitted not only light but also sound.

Table I shows the measured mean diameters of the products generated using different electrolyte concentrations. Part of the input electrical energy was converted to heat, and therefore, the solution temperature reached approximately 90 °C. A larger voltage was required for a lower electrolyte concentration because the liquid resistance increased. Therefore, the electric power required for maintaining the plasma had a similar value of 40 ± 5 W, although the electrolyte temperature and surface conditions of the electrode changed

slightly. At a electrolyte concentration of 1.0 kmol m^{-3}, the electric power was slightly less than 35 W owing to the lack of ignition.

Figure 2(a) shows plots of the mean diameter of the products against the applied voltage. The tendency of the results agreed with the data previously obtained by Toriyabe et al. by SEM, [10] although a different method was used to measure the particle size. The particle diameter decreased with decreasing electrolyte concentrations. It should be noted that the fiber optic dynamic light-scattering photometer used cannot exclude agglomerated nanoparticles completely in the size evaluation, and therefore, the actual mean diameter might be slightly small. Figure 2(b) shows plots of the mean diameter against the current density. The results revealed the linear relationship between the mean product diameter D_p (nm) and the current density J(A cm^{-2}) for electrolyte concentrations ranging from 0.001 to 0.5 kmol m^{-3}; $D_p = 76 \bullet J + 50$.

Figure 3 shows typical micrographs of the Ni products and electrode surface. The TEM observations shown in Figs. 3(a)-3(d) validate the mean diameter shown in Fig. 2 that was measured using a fiber optic dynamic light-scattering photometer. The same tendency was observed between the mean product diameter and the applied voltage. However, it should be noted that the smallest particle size observed by TEM was less than 10 nm. Figures 3(e)-3(i) show macroscopic SEM images of the Ni electrode surface after experiments. Obviously, many cracks were observed, in which larger particles were generated near larger cracks [see (e) and (f)] and smaller particles, near smaller cracks [see (g)]. The cracks grew along the electrode with increasing of electrolyte concentration owing to the resistance heating caused by an increase in current. These cracks were formed by thermal expansion. In contrast, no cracks were observed at the lowest electrolyte concentration of 0.001 kmol m^{-3} owing to a decrease in current. The microscopic SEM images shown in Figs. 3(j)–3(n) reveal that the surface became rougher at a higher electrolyte concentration owing to a smaller current density. In conclusion, a lower electrolyte concentration is effective for generating smaller particles owing to a decrease in electric current. Interestingly, we also discovered that regular patterns are always generated on the electrode surface for electrolyte concentrations ranging from 0.1 to 0.005 kmol m^{-3}. It is likely that nanoparticles were generated at pointed projections [see (i), (k), and (l)]. One particle was generated from one point. A large current concentrated at one point with increasing electrolyte concentration when the inflow of electric power is constant (40 W) and large particles were

generated with an increase in the temperature of the point. In contrast, many holes were observed on the surface at the lowest concentration of 0.001 kmol m^{-3}. This was most likely caused by the spark being electrically discharged, thus leading to the flow of a large current.

In summary, plasma electrolysis for synthesizing size-controlled Ni particles was studied. In this method, voltage was applied to both nickel and platinum electrodes that were immersed in NaOH electrolytes with concentrations ranging from 1.0 to 0.001 kmol m^{-3}. A larger voltage was required to maintain the plasma at a lower electrolyte concentration; for example, the voltage was 90 V for an electrolyte concentration of 0.5 kmol m^{-3} and it was 590 V for an electrolyte concentration of 0.001 kmol m^{-3}. Direct observation by SEM/TEM revealed that the products obtained were spherical at all electrolyte concentrations and that their size decreased with the applied voltage. The smallest particle observed was less than 10 nm in size. The surface of the Ni electrode became rougher at a larger electrolyte concentration owing to a higher current density. A larger voltage caused a smaller diameter; for example, the diameter was 148 nm for a voltage of 90 V, and it was 70 nm for a voltage of 590 V. We hope that these findings will lead to further developments in plasma electrolysis for the production of nanoparticles with advantages such as the ability to control the product size, use of simple equipment for easy mass production, and applicability to any electrically conductive metal/alloy.

1) J.-H. Jang and J. Lin: Surf. Coat. Technol. **202** (2008) 6136.
2) K. Takada, R. Ma, M. Osada, N. Ohta, L. Zhang, and T. Sasaki: J. Power Sources **146** (2005) 703.
3) B. Liu, Z. Hu, Y. Che, Y. Chen, and X. Pan: Appl. Phys. Lett. **90** (2007) 044103.
4) H. Muto, K. Miyajima, and F. Mafune: J. Phys. Chem. C **112** (2008) 5810.
5) A. Shimofusa, T. Kuga, O. Kido, H. Suzuki, Y. Saito, and C. Kaito: J. Phys. Soc. Jpn. **74** (2005) 2996.
6) Y. Kitamura, N. Okinaka, T. Shibayama, O. O. P. Mahaney, D. Kusano, B. Ohtani, and T. Akiyama: Powder Technol. **176** (2007) 93.
7) Y. Kitamura, N. Okinaka, O. O. P. Mahaney, D. Kusano, B. Ohtani, and T. Akiyama: J. Alloys Compd. **455** (2008) L1.
8) A. Hickling and M. D. Ingram: J. Electroanal. Chem. **8** (1964) 65.
9) K. Azumi, A. Kanada, M. Kawaguchi, and M. Seo: J. Surf. Finish. Soc. Jpn. **56** (2005) 232 [in Japanese].
10) Y. Toriyabe, S. Watanabe, S. Yatsu, T. Shibayama, and T. Mizuno: Appl. Phys. Lett. **91** (2007) 041501.
11) A. H. Nelson: AIAA J. **8** (1970) 1753.
12) K. Okazaki, Y. Mori, K. Hijikata, and K. Ohtake: AIAA J. **16** (1978) 334.
13) T. Mizuno, T. Akimoto, K. Azumi, T. Ohmori, Y. Aoki, and A. Takahashi: Jpn. J. Appl. Phys. **44**(1A) (2005) 396.
14) M. Kaszuba, D. McKnight, M. T. Connah, F. K. McNeil-Watson, and U. Nobbmann: J. Nanopart. Res. **10** (2008) 823.
15) A. J. Jin, D. Huster, K. Gawrisch, and R. Nossal: Eur. Biophys. J. **28** (1999) 187.
16) D. O. Neal, P. Harrip, G. Dragicevic, D. Rae, and J. D. Best: J. Lipid Res. **39** (1998) 2086.

Fig. 1. (Color online) (a) Schematic diagram of the experimental apparatus of plasma electrolysis for the synthesis of Ni nanoparticles, in which electrolysis solutions of NaOH with different concentrations from 1.0 to 0.001 kmol m^{-3} and dispersant of sodium dodecyl sulfate (SDS) with a concentration of 0.001 kmol m^{-3} were used. The cell was made of borosilicate glass with a capacity of 300 ml, with a 30 mm distance between two electrodes. (b) Histories of cell voltages in electrolysis solutions of different electrolyte concentrations, in which the voltage was applied at a rate of 0.1 V/s until ignition and then was kept at 40 W in electric power to keep plasma in 3.6 ks. (c) Photographs of electrode during plasma electrolysis at 0.05 kmol m^{-3}.

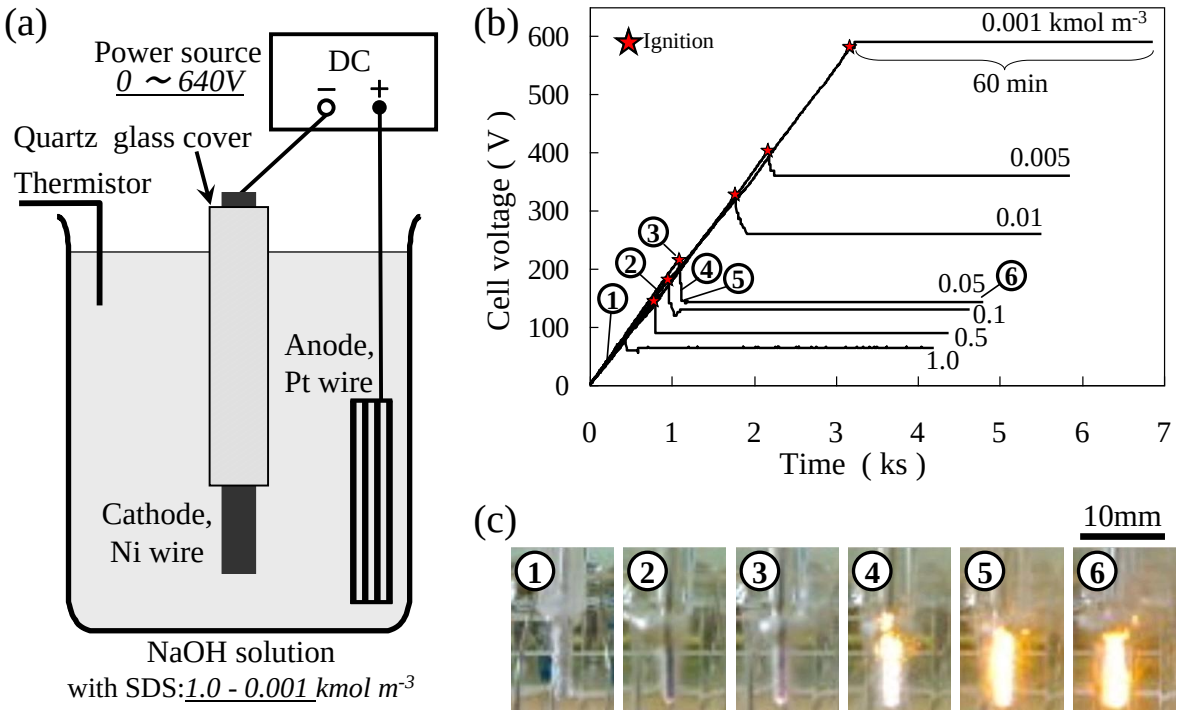
Fig. 2. Plots of mean diameter of the products passed through membrane with a pore size of 0.45 μm. Here, the error bar indicates the standard deviation. (a) Plots of mean diameter against voltage charged together with reported data of average diameter evaluated by SEM. (b) Plots of mean diameter against current density J. Current density was derived by dividing the average current during electrolysis at constant voltage by the surface area. The straight line approximation was found by least-squares fitting, and its equation is $D_p = 76 \bullet J + 50$ (nm). Here, R^2 indicates the coefficient of determination.

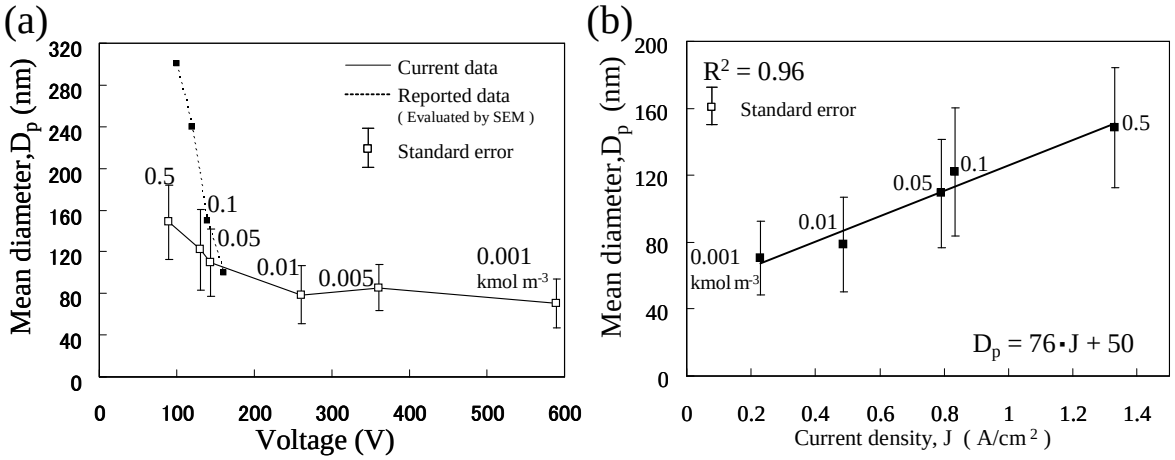
Fig. 3. Typical micrographs of Ni products and surface of electrode observed by TEM and SEM. [(a)-(d)] TEM images of Ni nanoparticles generated at different concentrations of electrolysis solution, in which the number of smaller particles increased with decreasing concentration of NaOH in electrolysis solution. [(e)-(i)] Macroscopic SEM images of Ni electrodes after the experiments. Note that cracks grew vigorously along the electrode with increasing electrolyte concentration. [(j)-(n)] Microscopic SEM images of Ni electrodes. With decreasing electrolyte concentration, the surface of the sample changed from rough to smooth owing to a smaller current density.

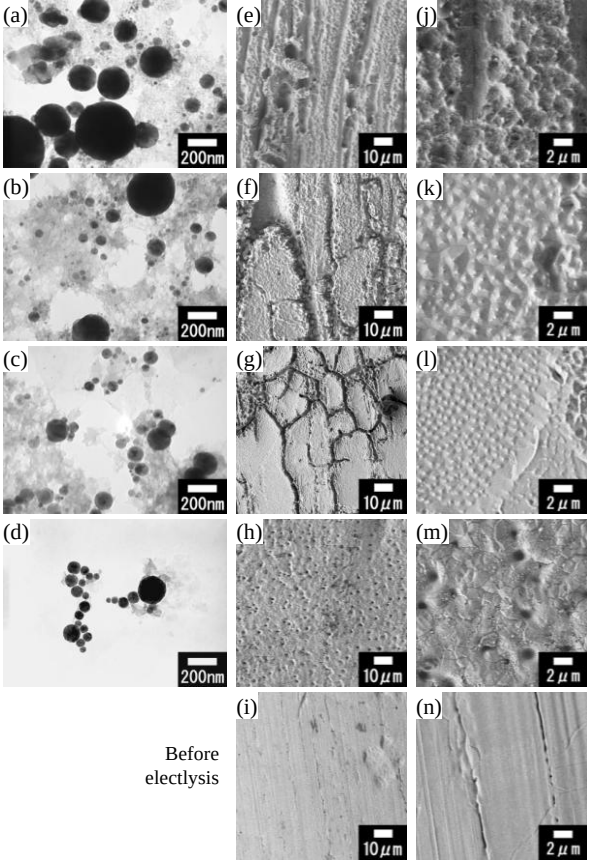
Table I. Mean diameters of products generated at different electrolyte concentrations, in which the voltage is controlled such that the electric power is within 40 ± 5 W.

Concentration (kmol m^{-3})	1.0	0.5	0.1	0.05	0.01	0.005	0.001
Voltage (V)	65	90	130	143	260	360	590
Current (A)*	0.47	0.43	0.27	0.25	0.16	0.12	0.07
Electric Power (W)*	31	39	35	36	41	43	44
Temperature (ºC)*	84	92	90	92	94	95	95
Mean diameter (nm)	137	148	122	109	79	86	70
Concentration (kmol m^{-3})	1.0	0.5	0.1	0.05	0.01	0.005	0.001

* 60 minutes average


(a)
Power source
0 ～640V
DC
−
+
Quartz glass cover
Thermistor
Anode,
Pt wire
Cathode,
Ni wire
NaOH solution
with SDS:1.0 - 0.001 kmol m-3
(b)
Ignition
0.001 kmol m-3
60 min
0.005
0.01
0.05
0.1
0.5
1.0
Cell voltage (V)
Time (ks)
(c)
10mm


(a)
Mean diameter,D_p (nm)
320
280
240
200
160
120
80
40
0
Current data
Reported data
(Evaluated by SEM)
Standard error
0.5
0.1
0.05
0.01
0.005
0.001
kmol m^{-3}
0
100
200
300
400
500
600
Voltage (V)
(b)
Mean diameter,D_p (nm)
200
160
120
80
40
0
R^2 = 0.96
Standard error
0.5
0.1
0.05
0.01
0.001
kmol m^{-3}
D_p = 76 · J + 50
0
0.2
0.4
0.6
0.8
1
1.2
1.4
Current density, J (A/cm^2)


0.5 kmol m-3
0.1 kmol m-3
0.01 kmol m-3
0.001 kmol m-3
Before electlysis
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
(j)
(k)
(l)
(m)
(n)
200nm
10μm
2μm