Classification and characterization of gold and nickel nanoparticles with a differential mobility analyzer

Yasutomo Naono, Sayuri Kawabata, Seung H. Huh, Atsushi Nakajima *

Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ka, Yokohama 223-8522, Japan

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Abstract

Ultrafine gold and nickel nanoparticles (NPs) were fabricated by pulsed laser ablation in helium gas, and the NPs 2–15 nm in diameter were selectively classified by an electrostatic size-selection technique employing a low-pressure differential mobility analyzer (LP-DMA). In the classification of the NPs, a chain of several gold NPs or doubly charged NPs were produced as well as singly charged spherical NPs. The morphological selection was performed with the LP-DMA, using a relationship in which the cross section of the spherical NP chains was governed by the product of the diameter and the length, instead of by the square of the diameter. Below a blocking temperature of about 100 K, the Ni NPs that were 3.1 nm in diameter exhibited ferromagnetism.

Keywords: Nanoparticles; Laser ablation; Differential mobility analyzer; Size selection; Magnetism; Gold; Nickel

1. Introduction

Recent advances in microminiaturization entails the further development of nanodevices, because the nanometer scale materials involved exhibit unique properties which differ considerably from those in bulk. Nanoparticles (NPs) in particular show a variety of size-dependent properties due to the dramatic changes occurring in the ratio of surface area to volume as a function of size [1–7]. Examples of recent research include discussion of the catalytic activity of gold (Au) nanostructures for the oxidation of carbon monoxide [1], surface-enhanced Raman scattering in coinage-metal NPs [2], a quantum dot effect in semiconductor NPs [3,4], the electric resistance of an Au nanorod [5], and the size-dependent magnetic [7] and structural evolution of such particles [8]. In addition, single-crystalline chemical growth has been reported in nanorods and nanowires [9,10]. Thus, a size dependency study of NPs and nanorods is crucial for both basic science and industrial applications.

Such studies require the development of a methodology for the preparation of well-defined nanostructured materials. Electrical mobility analysis methods, typified by the use of a differential mobility analyzer (DMA) [11], have recently provided an effective tool to control the size of NPs [12–15]. In particular, a low pressure differential mobility analyzer (LP-DMA) is beneficial when classifying monodispersed NPs in the gas phase. Seto and coworkers have reported the precise classification of various elements by the LP-DMA [12], but the shapes of the NPs were limited to spherical nanoparticles.

In this work, we present a new way to utilize the LP-DMA with a laser ablation source. As well as spherical Au NPs, anisotropic structures of a chain of several Au NPs were produced and morphologically selected with an LP-DMA in which chains of multiple NPs were produced in NP gas phase collisions. On the basis of an evaluation of the diameters and lengths of the Au NPs chains, an empirically modified rule for prolate spheroids is proposed.

2. Experimental section

The experimental set-up is schematically illustrated in Fig. 1. The apparatus is composed of the ablation chamber, the LP-DMA chamber (Vacuum Metallurgical Co., Ltd), and the deposition chamber. Before the experiments, the ablation chamber was evacuated to $1 \times 10^{-4}$ kPa using a turbo molecular pump. High purity helium gas (99.9999%) was then introduced into the ablation chamber by controlling the flow rate ($Q_a$ in Fig. 1) of 0.4–1.0 standard liters per minute (SLM) with a mass flow controller (MFC). A rotating target disk of gold or nickel (diameter 50 mm, 2 mm thickness, purity 99.95%) was vaporized with the second harmonic (wavelength...
of 532 nm, 20–40 mJ/pulse) of a Nd$^{3+}$:YAG laser (New Wave Research, Tempest-30Hz) in an ambient He pressure of 1.5–3 kPa. The metal NPs produced were transported through a stainless tube (length $Z_{300}$ mm, and bore diameter $Z_{10}$ mm) to the LP-DMA chamber by the He flow.

In the LP-DMA, charged particles were sorted by a helium sheath gas flow designated as ‘$Q_c$’ in Fig. 1 and an electric field generated by applying voltage ($V_{DC} = 0–150$ V) to an inside cylinder, where the direction of the sheath gas flow was perpendicular to that of the electric field. In this study, $Q_c$ was varied from 2.0 to 5.0 SLM, a level which was set to be five times larger than the helium gas flow rate into the ablation chamber, $Q_a$, (from 0.4 to 1.0 SLM); this setting is known to provide a good separation performance [16].

In general, electric mobility, $Z_{p}$, shows a distribution that depends on the experimental conditions. The median value of the electric mobility distribution of the classified NPs, $Z_{PC}$, is given by an equation including the applied voltage, $V_{DC}$, the sheath gas flow rate, $Q_c$, and the three dimensions of $L$, $R_1$, and $R_2$ in the DMA [11];

$$Z_{PC} = \frac{Q_c \ln(R_2/R_1)}{2\pi LV_{DC}}. \quad (1)$$

The dimensions of our DMA were $L = 10$ mm, $R_1 = 11$ mm, and $R_2 = 18$ mm, short enough to classify NPs 1–20 nm in diameter. The electric mobility, $Z_{p}$, is generally related to the diameter of the NPs, $d_{NP}$, as

$$Z_{p} = \frac{qeC_c}{3\pi\mu d_{NP}}. \quad (2)$$

where $q$ and $\mu$ are the number of electrical charges and the viscosity of the sheath gas. In Eq. (2), the Cunningham correction factor, $C_c$, for slip in gases is given by [17]

$$C_c = 1 + \frac{2\lambda}{d_{NP}}[1.257 + 0.40 \exp(-0.55d_{NP}/\lambda)], \quad (3)$$

where $\lambda$ is the mean free path of a gas molecule at standard state pressure. Since $\lambda$ for the helium of the sheath gas is 137 nm, Eq. (3) for NPs of $d_{NP} = 2–15$ nm can be simplified with $\lambda d_{NP} \gg 1$ as follows:

$$C_c = \frac{3.32\lambda}{d_{NP}}. \quad (4)$$

The sheath gas flow ($Q_c$) and the electrical field ($V_{DC}$), in particular, are crucial factors for the classification of NP diameter ($d_{NP}$), together with the shape of the analyzer. Their relationship is simply expressed as

$$V_{DC} = Q_c \times d_{NP} \times C_{DMA} \quad (5)$$

where the $C_{DMA}$ in this work was 0.332 for singly charged NPs ($q = 1$) in helium. For example, 20 V must be applied for the selection of NPs with a diameter of 3.5 nm when the $Q_c$ is 5.0.
SLM. When $Q_c$ is 2.0 SLM, NPs with diameters of 15.0 nm are classified by setting the voltage at 150 V.

In the deposition chamber, a Faraday cup was set below the outlet nozzle of the LP-DMA (inner diameter: 4.0 mm). Before deposition, the amount of nanoparticles classified was measured as an electric current by this cup, and, after the NP amount was optimized at about $1 \times 10^{10}$ per minute ($\sim 30$ pA), the classified NPs were deposited onto a grid for transmission electron microscope (TEM). After about 30 min of deposition, the morphology of the NPs was characterized by a field emission-transmission electron microscope (TEM; TECNAI F20 (PHILLIPS)). The size distributions of the NPs were determined from the TEM images and were fit by a log-normal function so that the classification capability might be evaluated, since the logarithm of the NP diameter is known to have a Gaussian distribution [18].

For Ni, furthermore, the magnetic properties of the classified NPs were characterized with a superconducting quantum interference device (SQUID) at 2–300 K. After the deposition of the Ni NPs for 60 min at a current of 40 pA, the deposited sample, in which the coverage was around 0.5, was taken out to the atmosphere, and its magnetic properties were measured with the SQUID.

3. Results and discussion

3.1. Classification of spherical Au nanoparticles and their chains

Fig. 2(a) shows a scanning electron microscope (SEM) image of the Au NPs obtained at the wall before entering the LP-DMA. Before the sorting, they exhibit a broad size

![Fig. 3. High-resolution TEM images of Au NPs and Au NPs chains sorted with LP-DMA (a) spherical Au NPs of $\sim 8.5$ nm in diameter, and (b)–(g) nanorod-like NPs chains composed of several NPs.](image_url)
distribution in the range from a few nanometer to 1 \( \mu \)m. The products on the wall include ablation debris from the target disk as well as the generated metal NPs. After the LP-DMA, however, only classified NPs are obtained with a relatively narrow distribution in the range from 2 to 16 nm in diameter.

Fig. 2(b) and (c) show, respectively, typical TEM images of 3.8 nm and \( \sim 15.4 \) nm Au NPs in diameter; most of the classified NPs have a spherical shape. Under the same laser fluence, a lower gas flow for the ablation chamber \( (Q_a) \) enhances the production of larger diameter NPs in the range of \( Q_a = 0.4–1.0 \) SLM, probably because the slower cooling rate of the helium gas favored the production of larger NPs. When the NP diameter was targeted to be 3.5 nm under a certain gas flow condition \( (Q_c: 1.0 \text{ SLM}, Q_a: 0.4 \text{ SLM}) \) for the LP-DMA, small Au NPs with an average diameter of 3.8 nm and a full-width-at-half-maximum (FWHM) of 1.1 nm, were cleanly separated. Similarly, larger Au NPs (average diameter, 15.4 nm and FWHM, 2.1 nm) were sorted by setting an appropriate gas flow condition \( (Q_a: 0.4 \text{ SLM}, Q_c: 2.0 \text{ SLM}) \). These results indicate that the sizes of the monodispersed NPs are very consistent with the diameter calculated from the electrical mobility expressions (Eqs. (1)–(5)).

As shown in Fig. 3(a), when the \( d_{NP} \) value of the LP-DMA was set to 8.5 nm under the low gas flow rate of \( Q_a = 0.4 \) SLM for the ablation chamber, the monodispersed, spherical Au NPs were well separated. However, as indicated in Fig. 3(b)–(g), when a higher flow rate of \( Q_a = 1.0 \) SLM was used, even with the setting of \( d_{SP} = 8.5 \) nm, nanorod-like NP agglomerates predominated. As mentioned before, the low flow rate of \( Q_a = 0.40 \) SLM promoted the production of larger NPs; for a \( d_{SP} = 8.5 \) nm, only the spherical Au NPs were produced. On the other hand, the high flow rate of \( Q_a = 1.0 \) SLM favored the production of smaller NPs, and therefore, when the classification diameter was set to be larger than the average diameter of the primary NPs, the major products were agglomerates. The agglomeration takes place via the Brownian motion of

![Fig. 4. High-resolution TEM images of Au NPs chains consisting of (a) single, (b) double, (c) triple, and (d) quadruple NPs, and, in (e)–(h), their averaged shapes, schematically illustrated with the diameter and length of the Au NPs chains. The black arrows indicate the individual NP units in the Au NPs chain.](image-url)
the highly concentrated NPs [19], and indeed, as is evident in Fig. 3(e)–(g), the NPs chains consist of several spherical NPs. In a further expanded view in Fig. 4(a)–(d), the high-resolution images show that the connected units are wholly metallic. Although several possible processes could conceivably generate the agglomerates made up of Au NP chains, the most plausible explanation is that the agglomerates were formed in the ablation chamber, because, as described below, their cross-sectional sizes seem almost constant.

Fig. 4(e)–(h) show the statistically averaged shapes of the primary nanoparticle diameters, the length, and their abundance ratios. As shown in the figures, the average NP diameter in the Au NP chains decreases with increases in the length (the number of component NPs); the average diameters are 8.5, 6.9, 5.9, and 5.0 nm for the chains consisting of 1–4 NPs, respectively, while the average lengths are 8.5, 11.7, 13.1, and 16.2 nm. Notably, the longer the length, the smaller the diameter for the classified NP chains. This trend strongly suggests that the NP chains were formed before the sorting with the LP-DMA, because if they were formed during and after the classification, the diameters of the Au NP chains would be constant regardless of the chain length.

The LP-DMA sorts particles on the basis of their electric mobility as determined by the collision cross-section of the particles for the sheath gas; this cross-section can be approximated by the hard-sphere collision cross-section. By means of a projection approximation, the cross-section was angle-averaged over all possible orientations of the NP about its center of mass, relative to the line of centers of the collision [20–22]. Analytical solutions exist only for a few, very simple structures, such as spheres and cylinders. The average collision cross sections, \( \sigma \), of a sphere of diameter \( 2r \) and a cylinder of length \( l \) and diameter \( 2r \) are analytically given in [20]:

\[
\sigma_{\text{sphere}} = \pi(r + r_{\text{He}})^2 \sim \pi r^2 \quad (6)
\]

and

\[
\sigma_{\text{cylinder}} = \frac{1}{2} \pi(r + r_{\text{He}})(l + r + 2r_{\text{He}}) \sim \frac{1}{2} \pi r(l + r), \quad (7)
\]

where \( r_{\text{He}} \) is the radius of a He atom. For the NPs, the minor contribution of \( r_{\text{He}} \) (0.14 nm) can be neglected. Since the NP chains obtained were prolate spheroids rather than cylinders, the cross section of the NP chains should be intermediate between a sphere (Eq. (6)) and a cylinder (Eq. (7)). Although

![Fig. 5. TEM images for Au NPs at \( d_{\text{NP}} = 11.0 \) nm and the size distribution (a) an overall TEM image, (b) an expanded view for the larger Au NP of 15.6 nm in diameter, and (c) histograms of the size with the fit of a log-normal function.](image-url)
the calculated \( \sigma_{\text{cylinder}} \) for all of the obtained NP chains give 30% larger values than those of the \( \sigma_{\text{sphere}} \) for \( d_{\text{NP}} = 8.5 \) nm, the constant values of \( \sigma_{\text{cylinder}} \) mean that the NP chains also were classified by their mobilities by the LP-DMA. Interestingly, a better reproducibility for the cross-section of the chains of prolate spheroids can be obtained from

\[
\sigma_{\text{spheroid}} \sim (1/2) \pi rl.
\]  
(8)

Eqs. (5) and (8), then, allow us to empirically write the equation of the mobility for prolate spheroids as

\[
V_{\text{DC}} = Q_{\text{C}} \times d_{\text{NP}} \times l \times C_{\text{DMA}}.
\]  
(9)

As well as the agglomerates, doubly charged NPs were produced and classified well. Fig. 5(a)–(c) show TEM images for Au NPs at \( d_{\text{NP}} = 11.0 \) nm, and their size distribution (Fig. 5(c)). All of the NPs were spherical, with a size distribution that was apparently bimodal at 11.2 and 15.6 nm, when relatively hot conditions were used—a flow rate of \( Q_{\text{a}} = 0.6 \) SLM and a higher laser fluence. The ratio of the diameters of the two peaks in the bimodal distribution corresponds to 1 : 1.4, which is in agreement with the calculated ratio of 1 : \( \sqrt{2} \) for the singly and doubly charged NPs. As shown in Fig. 5 (b), the expanded view for the larger Au NP appears uniform; therefore, we concluded that singly and doubly charged NPs coexist. In order to exclude multiply charged NPs, a relatively lower laser fluence seems preferable, an adjustment which provides a narrower size distribution for the primary NPs.

3.2. Magnetic properties of Ni nanoparticles

Similarly to the Au NPs, monodispersed spherical Ni NPs were well classified (Fig. 6(a)) by a setting of the \( d_{\text{NP}} \) value of the LP-DMA to 3.5 nm under a gas flow rate of \( Q_{\text{a}} = 1.0 \) SLM for the ablation chamber. As shown in Fig. 6(b), small Ni NPs with an average diameter of 3.1 nm were well-selected, where the full-width-at-half-maximum (FWHM) was 1.4 nm.

Under almost the same conditions as those illustrated in Fig. 6(a), a sample of Ni NPs was prepared with the deposition time of about 60 min. (coverage, \( \sim 0.5 \)). The magnetic properties of the Ni NPs were characterized by SQUID measurements of the hysteresis loop and zero field cooling/field cooling (ZFC/FC). Fig. 6(c) shows the magnetization versus magnetic-field curves of the Ni NPs, measured at 2 and 300 K. At low temperatures, the Ni NPs sample exhibited hysteresis, indicating the existence of ferromagnetism (FM). However, at room temperature, the FM hysteresis seemed to have disappeared, and more insight could be obtained from the measurements of temperature-dependent magnetization, \( M(T) \).

Fig. 6(d) shows the \( M(T) \) curves of the Ni NPs measured in \( H = 100 \) Oe. In a the ZFC experiment, the sample was first demagnetized at a very high temperature and cooled down in zero magnetic field. Then, at a very low temperature, a small external magnetic field of \( H = 100 \) Oe was applied and the sample was heated up until well above the blocking temperature. In the subsequent FC experiment, the small magnetic field of \( H = 100 \) Oe was maintained and the sample was cooled down again. During the whole ZFC/FC experiment, the magnetization \( M \) along the field was measured. In a typical ZFC measurement, the ZFC magnetization increased with increasing temperature until the blocking temperature, \( T_{\text{B}} \), was reached. Above \( T_{\text{B}} \), in the superparamagnetic regime, the ZFC magnetization decreased monotonically with rises in temperature. In the FC experiment, the FC magnetization coincided with the ZFC one until the blocking temperature was reached. This pattern occurred because, above \( T_{\text{B}} \), the system was able

Fig. 6. TEM image (a) and the size distribution (b) of Ni NPs \( \sim 3.1 \) nm in diameter after classification by LP-DMA. The histogram of the size distribution was fitted by a log-normal function. The SQUID results of (c) hysteresis loop at 2 and 300 K and (d) zero field cooling/field cooling (ZFC/FC) in the range of 2–300 K are also shown. Below a blocking temperature, \( T_{\text{B}} \), around 100 K, the sample of the Ni NPs exhibited ferromagnetism (FM).
to reach thermal equilibrium within the time lag between the measurements, and tended to show a constant value at low temperatures. In particular, the ZFC/FC curves at $H = 100$ Oe (Fig. 6(d)) indicate two facts: (1) superparamagnetism (SPM) is present at room temperature and (2) a blocking temperature, $T_B$, exists around 100 K. This result is consistent with the magnetic properties of Ni NPs in silica glass [23] where the Ni NPs (3 nm in average diameter) exhibited superparamagnetism at room temperature. It is noteworthy that the Ni NPs sample was exposed to air when it was installed in the SQUID equipment, and at that point, the surface of the Ni NPs probably became partially covered with oxides. Although the magnetic properties of the clean Ni NPs should be examined without the air exposure, this experiment has clearly demonstrated that the sample preparation used with the LP-DMA can provide a sufficient amount of NPs for investigation of magnetic properties.

4. Conclusions

The low-pressure differential mobility analyzer (LP-DMA) enabled us to produce and classify the spheres and prolate spheroids of Au NPs, by controlling the flow rate for the ablation chamber. In the analysis of the shapes, the cross section of the NP spheroids is empirically given by the product of the diameter and the length. The magnetic properties of Ni NPs 3.1 nm in diameter exhibit superparamagnetism at room temperature and ferromagnetism below a blocking temperature of about 100 K. These results demonstrate that NPs classification with the LP-DMA enables us to investigate the intrinsic physical and chemical properties of naked NPs with a narrow size distribution.

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