SIZE DISTRIBUTION ANALYSIS OF NANOPARTICLES USING SMALL ANGLE X-RAY SCATTERING TECHNIQUE

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Small angle X-ray scattering (SAXS) technique was used to determine size distributions of various nanoparticles. SAXS experiments were performed in both the transmission geometry to measure particles dispersed in solvents or bulk films and the reflection geometry to measure particles dispersed in thin films deposited on substrates. The X-ray size distributions agreed well with the results from TEM experiments. The size distribution of subnanoclusters, which could not be estimated using TEM, was successfully analyzed using SAXS.

1. Introduction

With recent improvements in nanotechnology, a large variety of nanoparticles have been synthesized. These particles are widely utilized in a large number of applications, including ultrafine wiring, light emitting devices, catalysts, fuel cells, covering materials, adhesion bond, abrasives, ink, medicines in drug delivery system (DDS), real-time PCR kit. However, techniques for evaluating nanoparticles are still in the developing stage. Although there are many techniques for size determination, each particular method usually has both advantages and disadvantages. Equipment must be selected that is appropriate to the shape, state, and size of the sample to be started. The most popular analytical technique is transmission electronic microscope (TEM), whose unique feature is the ability to give information on real images as well as size. However, understanding size distribution using TEM is difficult because a large number (hundreds) of particles is necessary to assure a reliable distribution. Further, manual procedures are usually necessary for the measurement of particles with sizes in 1 to 2 nm range or less, because it is very difficult to estimate the size distribution with image processing alone. Other techniques for particle size evaluation are: dynamic light scattering (DLS), laser diffraction, differential mobility analyzer (DMA), and time-of-flight secondary ion mass spectroscopy (TOF-SIMS). The advantages and disadvantages of these techniques are listed in Table 1.

This report introduces a new method of size distribution analysis: the small-angle X-ray scattering (SAXS) technique. SAXS is preferable to other methods because nondestructive and rapid measurements can be performed for a variety of samples such as thin films, powder, solution, bulk films, etc. SAXS can be readily applied to particles in the range from 1 to 100 nm, although measurements outside this range are also possible. Particles of size ca. 1 to 10 nm in particular can be analyzed with higher accuracy compared to other techniques. (Particles in this range will be referred to as “small” particles.) In this paper, the principle of size distribution analysis will be described, and SAXS results of various nanoparticles will be examined.

2. Principles of Size Distribution Analysis

X-ray scattering occurs when particles differing in electron density from their surrounding matrix are irradiated. The scattering profile is provided by the square of the absolute Fourier transform of electron density fluctuations, which depends on the form of particles:

\[ I(q) = |F(q)|^2 \]

\[ F(q) = \int V \Delta \rho(r) \exp[iqr] dV \]  

(1)
that these sizes are distributed according to the form factor $F(q, D)$ is calculated using a simple integral as follows.

\[
|F(q, D)|^2 = |\Delta \rho|^2 \left| \frac{4\pi}{q^3} \left( \sin \left( \frac{qD}{2} \right) - \frac{qD}{2} \cos \left( \frac{qD}{2} \right) \right) \right|^2
\]

(2)

where $q$ is the scattering vector, defined by eq. (3):

\[
q = \frac{4\pi}{\lambda} \sin \theta
\]

(3)

$\theta$ is the scattering angle, and $\lambda$ is the wavelength of the X-rays. Generally there is a range of particle sizes in any given sample. Assume that these sizes are distributed according to the $\Gamma$-distribution function $P(D, D_0, \sigma)$, represented by eq. (4). The scattering intensity is then given by eq. (5):

\[
P(D, D_0, \sigma) = \frac{1}{\Gamma(1/\sigma^2)} \left( \frac{1}{\sigma^2 D_0} \right)^{1/\sigma^2} D^{-1+1/\sigma^2} \exp \left[ - \frac{D}{\sigma^2 D_0} \right]
\]

(4)

\[
|F(q, D_0, \sigma)|^2 = |\Delta \rho|^2 \int_0^\infty \frac{4\pi}{q^3} \left( \sin \left( \frac{qD}{2} \right) - \frac{qD}{2} \cos \left( \frac{qD}{2} \right) \right) \left| P(D, D_0, \sigma) \frac{D^3}{D_0^3} \right| dD
\]

(5)

where $D_0$ is the average diameter of particles, and $\sigma$ is the normalized variance. Non-linear least squares can be used to refine these two parameters by comparing raw data with simulated data. These refined parameters give a tangible distribution graph of eq. (4). The factor $D_0^3/D^3$ is introduced to represent the distribution in terms of volume fraction. When a distribution obtained using SAXS is compared to one obtained using TEM, the scattering intensity should be calculated with a $D_0^3/D^3$ of 1.0.

When the SAXS measurements of nanoparticles are carried out in the transmission geometry, the scattering intensity is expressed by eq. (5). It should be noted that thin film materials containing dispersed nanoparticles are often used as actual samples.

Applying SAXS technique to thin films whose thickness is dozens or hundreds of nanometers, however, is limited when there are not enough scatterers, or when the measurement cannot be performed in the transmission geometry because X-rays cannot transmit through the substrate. In these cases, SAXS patterns can be measured in the reflection geometry to avoid these limitations [1, 2]. In the reflection geometry, the irradiated area is proportional to $1/\sin \theta$ (where $\theta$ is the angle between incident X-rays and the sample surface). The grazing incident beam allows more scatterers to contribute to the scattering intensity, and more importantly, X-rays are not absorbed by the substrate. On the other hand, in the reflection geometry, the incident X-rays are affected by multiple reflections and refractions at the film surface and interfaces. The correction of SAXS intensity measured in the reflection geometry, therefore, is performed using the distorted wave Born approximation (DWBA) [3, 4] as described in references [1, 2, 6].
3. Examples

It is well-known that physical properties of nanoparticles are quite different from the same compound in bulk. This is because the numbers of atoms on the surface of nanoparticles are relatively large. In recent years, material sciences have been very active in the discovery of new nanoparticle properties and their applications. Because the surface effect is size-dependent, particle size must be determined before materials can be developed further.

Analysis results of gold and copper nanoparticles were obtained using SAXS in the transmission geometry and are described in sections 3.1 and 3.2. Those of nickel nanoparticles in thin films obtained using SAXS in the reflection geometry are given in section 3.3. The SAXS measurements were performed using a Rigaku ATX diffractometer and a rotating anode X-ray generator operated at 50 kV and 300 mA.

3.1. Size Distribution Analysis of Gold Nanoparticles

Historically, gold nanoparticles have been used for decorating stained glasses and chinas. Gold shows a distinct plasmon resonance peak in the UV–VIS spectrum. Recently there has been an increased interest in this optical property because of potential applications in new censors or optical devices. In addition, gold nanoparticles are now used in clinical practice because they are not harmful to the human body. Gold nanoparticles are one of the most important metallic particles, and are expected to be used much more widely in the future.

Gold has a high scattering intensity. Its nanoparticles are almost round, and are usually surrounded by a protective coat of organic molecules so that they can be stably dispersed in solvents. Because of these features, gold nanoparticles are the most suitable for analysis using SAXS.

Figure 1 shows TEM images of the gold nanoparticles.
nanoparticles Au 15 nm and Au 35 nm. SAXS patterns of these particles were measured and their observed profiles are shown in Fig. 2. The black lines are obtained from Au 15 nm and the gray lines from Au 35 nm. In this and subsequent intensity plots, thin lines represent raw data; thick lines represent simulated data. Simulated data were obtained from the average diameter and dispersion of the particles. In general, a concentration of ca. 1.0 wt% of particles is necessary for a SAXS measurement. The scattering intensity of these two samples was observed even though the concentrations were both very low (0.005 wt%). The size distributions of the particles were obtained by analyzing the scattering profiles (Fig. 3). The average diameters were estimated to be 16.4 nm for Au 15 nm

and 36.0 nm for Au 35 nm, which agree with the TEM images.

The following describes analysis results of small gold nanoparticles. The absorption and plasmon resonance spectra of small gold nanoparticles are highly sensitive to particle size. In search of new discoveries, research on gold nanoparticles has been focused mostly on small sizes. SAXS technique is ideal for analyzing small particles, therefore it is expected to be used widely in size distribution analysis of gold and other nanoparticles in this range.

Figure 4 shows the TEM images of gold nanoparticles (DT@Au A and DT@Au B) with different size distributions [5]. The SAXS profiles shown in Fig. 5 were obtained from the gold nanoparticles dispersed in toluene. The black lines are DT@Au A, and the gray lines are DT@Au B. The measured profile of DT@Au A in particular fits the calculated profile almost perfectly.

In Figs. 6 and 7 SAXS results are overlapped on the TEM histograms of DT@Au A and DT@Au B, respectively. It should be noted that the resolution of the SAXS experiment is much greater than TEM, especially when particle diameters are small (as is the case for DT@Au A).

Results of the size distribution analysis of gold subnanoclusters is described below. SAXS profiles of these clusters are shown in Fig. 8. In this case TEM was not able to estimate the size distribution because the cluster sizes were too small. Figure 9 shows the size distribution obtained from the subnanocluster scattering pattern.

As described above, the physical properties of nanoparticles are known to be size-dependent. Efforts are being made currently to synthesize uniform particles in order to control the

Table 2. Size distribution analysis of Au 15 nm and Au 35 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter $D_0$</th>
<th>Dispersion $\sigma$</th>
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<tbody>
<tr>
<td>Au 15 nm</td>
<td>16.4 nm</td>
<td>0.32</td>
</tr>
<tr>
<td>Au 35 nm</td>
<td>36.0 nm</td>
<td>0.23</td>
</tr>
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</table>

Fig. 3. Size distribution of Au 15 nm and Au 35 nm.

Fig. 4. TEM images of gold nanoparticles. (a) DT@Au A, (b) DT@Au B.
properties. On the other hand, nanoparticles are historically separated by size using the high-performance liquid chromatography (HPLC) and the gel permeation chromatography (GPC). Figure 10 shows a gel permeation chromatogram of gold nanoparticles with a wide distribution of 1.0 to 5.0 nm. The size distributions of fractions a, b and c were estimated using the SAXS method (Fig. 11).

In summary:
1. SAXS can be used to measure a wide range of nanoparticle sizes (from 1 to several tens of nanometers).
2. Small particles can be analyzed very precisely using SAXS.
3. The SAXS method can estimate the size distribution of subnanoclusters, which is difficult to estimate using TEM images. In general, SAXS measurements for size distribution analysis can be done within a few minutes. It is a straightforward measurement and does not require special sample preparation. For the gold nanoparticles described above, nanoparticles solutions were simply measured directly from glass capillaries. The measurement can be carried out at room temperature without sealing the capillaries unless the solvent is known to vaporize very quickly. Therefore, one can use SAXS method for the evaluation of nanoparticles in the same way one uses NMR or IR methods. Thus, SAXS technique, which estimates size distributions easily and quickly, is expected to gain popularity as a method of choice for the synthesis and characterization of nanoparticles.

3.2. Copper Nanoparticles Dispersed in Polyimide Films

This section describes the size distribution analysis of copper nanoparticles in polyimide films. Particles in films cannot be evaluated using DLS or DMA. The only evaluation method currently being used is cross-sectional TEM images. In order to obtain cross-sectional TEM images, however, samples must be prepared by sectioning into very thin slices using a microtome technique, and may take up to two days. Figure 12 shows the cross-sectional TEM images of copper nanoparticles dispersed in polyimide films. The advantage of SAXS technique is that the measurement can be done simply by placing the film sample onto the sample stage as is (without any preparation). This is possible because X-rays transmit through thin films easily. Figure 13 shows size distributions of copper nanoparticle samples estimated using SAXS. These are consistent with the TEM images.

3.3. Evaluation of Size Anisotropy of Nickel Nanoparticles in Thin Films

This section describes the size distribution analysis of nickel nanoparticles dispersed in carbon thin films. Since the magnetic properties of nickel nanoparticles are size-dependent, size

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**Table 4.** Size distribution analysis of fractions a, b, and c.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter $D_0$</th>
<th>Dispersion $\sigma$</th>
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<tbody>
<tr>
<td>a</td>
<td>3.35 nm</td>
<td>0.13</td>
</tr>
<tr>
<td>b</td>
<td>2.75 nm</td>
<td>0.20</td>
</tr>
<tr>
<td>c</td>
<td>2.19 nm</td>
<td>0.27</td>
</tr>
</tbody>
</table>

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**Fig. 10.** Gel permeation chromatogram of gold nanoparticles.

**Fig. 11.** Size distribution for fractions a, b, and c.

**Fig. 12.** Cross-sectional TEM images of copper nanoparticles dispersed in polyimide film.
distribution analysis plays an important role in the characterization of this material.

Figure 14 shows SAXS patterns of nickel nanoparticles. The black pattern was obtained using an out-of-plane measurement, where the scattering vector is in the direction almost normal to the sample surface. The gray pattern was obtained using an in-plane measurement, where the scattering vector is in the direction parallel to the surface. Figure 15 shows the size distributions of the nickel particles estimated from the SAXS patterns [6].

The size distribution of nickel particles along the direction normal to the surface is almost the same as that along the direction parallel to the surface (Fig. 6). This indicates that there is no anisotropy in the size distribution of nickel particles. This type of anisotropy analysis is very helpful in the study of thin film devices.

4. Concluding Remarks

The SAXS size distribution analysis method can be applied to materials with small electron density differences. Even if the elements of particles and matrix are the same (diamond particles in graphite, for example), this analysis can still be performed. Nano-pores, as well as nanoparticles, are often good applications for the SAXS method. Although TEM and gas adsorption are the currently prevailing methods for pore-size distribution analysis, both have significant inconveniences when measuring thin film samples. However, recently it has been reported that SAXS can easily estimate the pore-size distribution in porous low-k film [1]. TEM or gas adsorption is a destructive measurement, whereas, SAXS patterns can be measured nondestructively and quickly in the same way as in the sections 3.1, 3.2 and 3.3.

The shapes of the particles described here are spherical or almost spherical. According to recent reports, core-shell particles built with two or three materials and long particles called nano-rods have been developed. The particles with non-spherical shape could be characterized by creating a new equation corresponding to each shape instead of eq. (2). In addition, if the real distribution does not obey the $\Gamma$-distribu-

![Fig. 13. Size distributions of copper nanoparticles annealed at 250°C and 400°C.](image1)

![Fig. 14. SAXS patterns of nickel nanoparticles obtained using out-of-plane and in-plane measurements.](image2)

![Fig. 15. Size distributions of nickel nanoparticles measured along the direction normal to the surface (out-of-plane) and along the direction parallel to the surface (in-plane).](image3)

Table 5. Size distribution analysis of copper nanoparticles dispersed in polyimide film.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Average diameter $D_0$</th>
<th>Dispersion $\sigma$</th>
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<tbody>
<tr>
<td>250°C</td>
<td>4.07 nm</td>
<td>0.20</td>
</tr>
<tr>
<td>400°C</td>
<td>9.06 nm</td>
<td>0.15</td>
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Table 6. Size distribution analysis of nickel nanoparticles dispersed in thin film.

<table>
<thead>
<tr>
<th>Scattering vector</th>
<th>Diameter $D_0$</th>
<th>Dispersion $\sigma$</th>
</tr>
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<tbody>
<tr>
<td>Normal to surface</td>
<td>5.82 nm</td>
<td>0.47</td>
</tr>
<tr>
<td>Parallel to surface</td>
<td>5.80 nm</td>
<td>0.42</td>
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</table>
tion function, better analysis could be done by preparing an appropriate distribution function in lieu of eq. (4). Various kinds of nanoparticles are now being developed. The simple, rapid and nondestructive SAXS method is proving to be an essential tool in evaluating nanoparticles in the future.

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References