Particle Characterization of Nanoscale Materials using Dynamic and Static Light Scattering

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ABSTRACT

Novel materials with single particle dimensions at the nano scale are submitted for analysis to our applications laboratory on a regular basis. These samples include nanotubes, buckyballs, quantum dots and various metal oxides. Determining the proper dispersion and test conditions to characterize nanomaterials is often challenging. This poster summarizes our experiences and the general methodology devised for handling unknown materials of reported "nano-scale" size.

Keywords: particle size analysis, dynamic light scattering, carbon nanotubes, buckyballs, quantum dots.

1 TECHNIQUE SELECTION

The particle characterization tools within our laboratory include dynamic, static, & electrophoretic light scattering with a Zetasizer Nano ZS system, laser diffraction with a Mastersizer 2000, automated image analysis with a Morphologi G2 (dry analysis) and a FPIA3000 (wet analysis), and visual inspection. Most nanosized materials are measured using dynamic light scattering with the Zetasizer Nano system. Dynamic light scattering (DLS), also known as photon correlation spectroscopy (PCS) and quasi-elastic light scattering (QELS) provides many advantages as a particle size analysis method. DLS is a non-invasive technique that measures a large population of particles in a very short time period, with no manipulation of the surrounding medium. Modern DLS instruments can measure particle sizes as small as 0.6 nm and as large as 6 um, across a wide range of sample concentrations. Because of the sensitivity to trace amounts of aggregates and the ability to resolve multiple particle sizes, DLS is ideally suited for nanoscale particle size analysis.

When unknown materials of reported nanoscale size enter our lab visual inspection can often provide a good indicator of the actual size of the particles. Particles below 100 nm should not settle at a rate detectable by visual inspection. Many allegedly nanosized samples arriving in our laboratory have settled during shipment. The presence of visible sediment at the bottom of sample containers causes concern regarding either the size of the particles or the state of aggregation. By using Stokes law and tabulating settling rates as a function of density as shown in Table 1 it is possible to quickly determine if the current particle size is indeed in the expected nanoscale range. As is evident from the data in Table 1, samples of particle size < 100 nm will take anywhere from 13 days to 3.5 years to settle, confirming the expectation that visual inspection can be used to quickly confirm the presence of particle sizes > 100 nm in the sample.

Size	ρ (Material)	Time to settle 1 cm
		minutes (days)
0.01μm	2500	1815494.39 (1261)
0.1μm	2500	18154.94 (13)
1μm	2500	181.55 (0.13)
10μm	2500	1.82
100μm	2500	0.02

Table 1: Sedimentation rate as a function of size & density

Although the dynamic range of DLS better suits nanosized particles, laser diffraction is often employed when the particle size proves experimentally to be greater than 1 micron. It is usually possible to inspect the correlation function from DLS to determine when the size is greater than the upper range of this technique as seen in Figure 1. The correlation function of two size measurements for sample Mn is shown in Figure 1. The unfiltered data shows number fluctuations evidenced by "spikes" in the baseline at correlation times > 1,000,000 micro-seconds that are consistent with the large visible aggregates in the samples, which were imaged with a microscope. In the graph, we observe that the aggregates can be removed with a filter but no particles are left in the suspension. If a 0.45μm filter removes all particles, then there are too few or no particles below 0.45μm in size to perform the experiment.

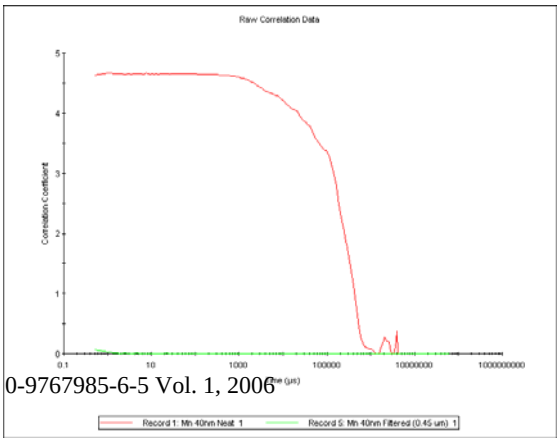

Figure 1: DLS correlation function w&w/o filtering.

Figure 2 shows an over-plot of four pre-sonication results for sample Mn analyzed using laser diffraction. The size results are consistent with the large visible aggregates in the samples, predicted from the DLS results and confirmed with digital microscopy.

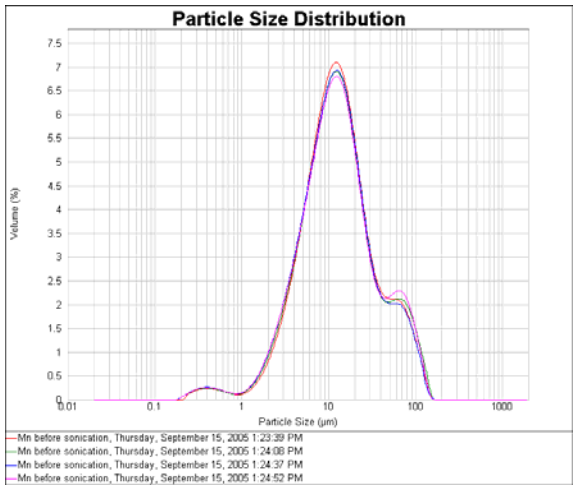

Figure 2: Sample results using laser diffraction.

2 SAMPLE PREPARATION

Any particle characterization tool will measure the sample in the state as it is introduced to the system. Many of the nanoparticles seen in our lab arrive in an agglomerated state and require effort to disperse the particles to their primary state. The tools used to aid dispersion include surfactants, dilute acid and ultrasonic energy, with the formulation recipe and dispersion procedures being as important as the dispersant selection. Consider for example, the variety in the procedures found to be effective for the dispersing of Molybdenum and Aluminum powder samples, ultimately measured by dynamic light scattering.

Procedure 1: One-half gram aluminum sample was wetted with dilute HCl and dispersed into a solution of dilute surfactant and electrolyte. The suspension was then sonicated for 30 minutes using a 600W ultra-sonication probe.

Procedure 2: One-half gram aluminum sample was also wetted with dilute NaOH (pH 10 and 8) and dispersed into a solution of dilute surfactant and electrolyte.

Procedure 3: One-half gram of molybdenum was wetted with dilute H_2S0_4 and dispersed into a solution of dilute surfactant and electrolyte. The suspension was then sonicated for 20 minutes using a 600W ultra-sonication probe.

Procedure 4: One-half gram of molybdenum was wetted with dilute Aqua Regia (mixture of HNO_3 and HCl).

Procedure 5: One-half gram of molybdenum was dispersed in a suspension of surfactant and electrolyte and then centrifuged. The supernatant was analyzed.

Figure 3 shows example dynamic light scattering results measured for sample Procedure 5:

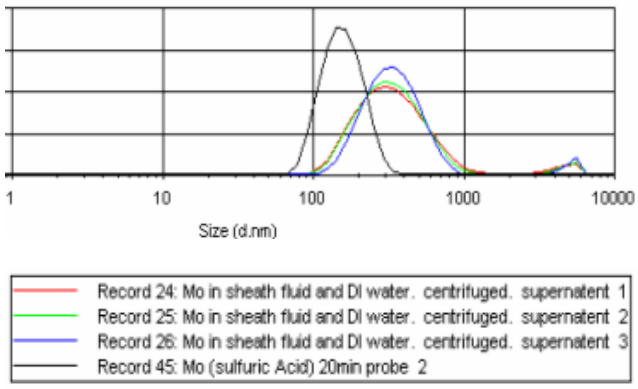

Figure 3: Effect of sample preparation on molybdenum.

3. NANOTUBES

In dynamic light scattering, particle size is not directly measured, but is calculated form the measured Brownian motion (diffusion coefficient) of the sample. The size reported from DLS is representative of the size of a hypothetical sphere that diffuses at the same rate as the particles being measured. DLS measurements of nanotubes and rods then become particularly challenging, in that they are clearly non-spherical. However, DLS can still provide useful information about nanotubes, especially if a-priori information is available.

A sample of CdSe nanorods dispersed in hexane, and described by the vendor as having dimensions of 4 nm wide and 25 nm long was submitted for DLS analysis to our application laboratory. The Z average size, or hydrodynamic radius (R_H), measured for the nanorods was 7.2 ± 0.2 nm. As shown in the upper half of figure 4 below, this size is significantly larger than the equivalent volume spherical size of a 4 x 25 nm nanorod of $R_{sp} = 4.4$ nm.

According to Perrin theory, differences between the hydrodynamic and the equivalent volume sizes are a consequence of both solvation and shape effects (figure 4). For rod shaped particles, both of these effects can be predicted and compensated for, using a prolate ellipsoid model.[(Cantor)] From Perrin theory, the axial ratio determined from DLS measurements of the CdSe nanorods is 11.22,

which differs significantly from the geometrically calculated axial ratio of 6.25 (= 25/4) for a *single* nanorod. However, if a bundle of two rods, or a dimerized system, is assumed, both the axial ratio and the reported rod length are consistent with measured DLS results, which predict an axial ratio of 5.2 and a rod length of 25.5 nm.

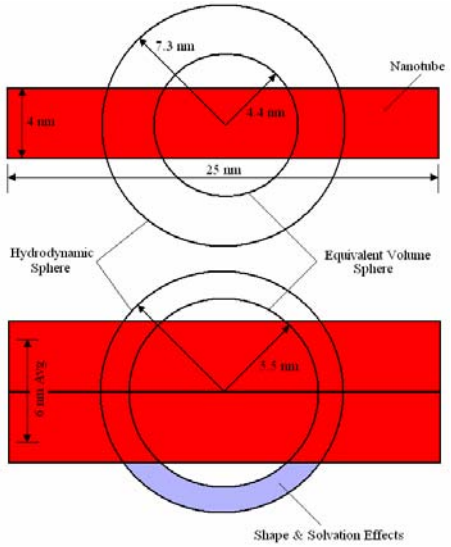

Figure 4: Hydrodynamic and the equivalent volume sizes of nanotubes.

4 BUCKYBALLS

The analyses of two fullerene C60 samples in corn oil, vendor identified as sonicated and unsonicated, was conducted, again using dynamic light scattering. Here the Zetasizer Nano ZS and the DLS technique were employed to study the affects of sonication upon the dispersion of the sample. Measurements were collected using the automatic mode of the Zetasizer Nano software, with the laser attenuation, measurement position, and sample measurement time being automatically optimized for maximum confidence in the analysis results. Measurement reproducibility was verified by collection and comparison of sequential measurements. High sample concentrations resulted in a "near the cell wall" measurement position being selected by the software for both C60 samples. This unique capability of the Zetasizer Nano system accommodates high sample concentration measurements by minimizing multiple scattering effects.

The dynamic light scattering results collected for the sonicated and unsonicated C60 samples are given in table 2 where the polydispersity index is equivalent to the relative variance, $(\sigma/Z_{Avg})^2$, of the size distribution.[(ISO13321)] As seen in the table 2 results, along with intensity particle size distributions shown in figure 5, sonication leads to a reduction in both the average size of the C60 dispersions and the polydispersity or width of the size distribution. These results provide clear evidence that the unsonciated sample is aggregated, and that sonication can be used to help break up the aggregates.

Sample Name	Z-Ave (nm)	Polydispersity Index	Diffusion Coeff. (μ^2/s)
Buckyball Sonicated	260	0.165	0.0308
Buckyball Unsonicated	328	0.354	0.0244

Table 2: Particle size of Buckyballs with and without ultrasound

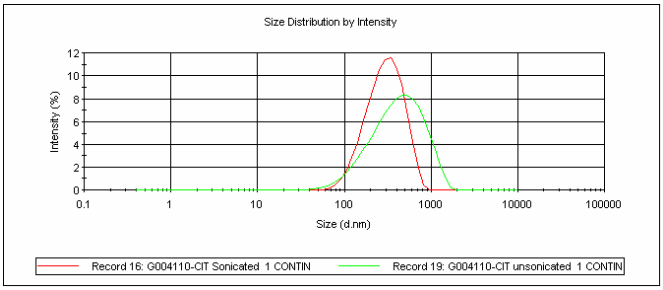

Figure 5: Particle size plots of Buckyballs with and without ultrasound.

5 METAL OXIDES

Nanoparticles synthesized from metal oxides are also routinely measured by dynamic light scattering techniques. Table 3 and figure 6 show the Z average & polydispersity index and the intensity particle size distributions measured for recent metal oxide samples submitted to our laboratory for analysis. The goal of the analysis was to establish whether or not DLS could be used to identify differences in the preparation conditions of the metal oxide samples. As seen in table 3 and figure 6, differences are clearly identifiable from the DLS measurement results.

	Z-average (nm)	Polydispersity Index PDI
Sample 1	72	0.274
Sample 2	258	0.125
Sample 3	245	0.252
Sample 4	190	0.258

Table 3: DLS results for metal oxide sample

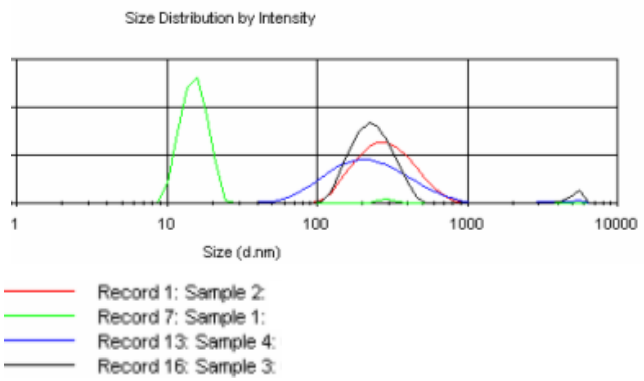

Figure 6: DLS results for metal oxides

CONCLUSION

A variety of sample techniques and analytical tools were applied to unknown samples with sizes expected in the nanoscale range. Many samples required changes in surface chemistry or the application of ultrasonic energy to disperse the samples to the primary particle size range. Dynamic Light Scattering has proven to be an effective tool for particle size analysis in the 1 – 100 nm size range where most nanosized materials can be found.

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