Nanoparticle Characterization Using Light Scattering Technologies

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ABSTRACT

Characterization of various nanoparticles is on the center stage in nanotechnology development. The subjects for nanoparticle characterization are focused on particle size and particle surface charge determination. The latest development in particle size analysis using dynamic light scattering and surface charge determination using electrophoretic light scattering for nano or even sub-nano particles in concentrated suspension is summarized.

Keywords: particle sizing, zeta potential, concentrated suspension, light scattering, PCS

1 SIZE ANALYSIS

For size analysis of dry nanoparticles transmission electron microscopy (TEM) or scanning electron microscopy (SEM) and small angle X-ray scattering (SAXS) are the only viable choices. Microscopic methods are accurate with high resolution, can provide shape information, and are often the final judgment for standard reference materials. In most cases, they only yield information from 2-D projected areas of particles. Particle orientation in the prepared sample can alter the result significantly. The biggest drawback is that in spite of modern image analysis means the number of particles in focus that can be inspected in any field of view is limited. Thus, for a polydisperse sample, an adequate statistical representation of entire sample can be an exhaustive, if not impossible, task. In addition, the analysis process is slow and expensive.

Dynamic light scattering (DLS) that utilizes time variation of scattered light from suspended particles in liquid under Brownian motion to obtain their hydrodynamic size distribution is the most popular technology in sizing nanoparticles. DLS has been used to measure macromolecules and small particles in dilute suspension since coherent light sources, i.e., commercial lasers, became available in the 1970's [1]. Lately, demand arises for measuring smaller particles in nanometer range that requires instruments being more sensitive in picking up weak scattering signals from small particles or molecules, and for measuring particles in concentrated suspension that requires instruments being able to avoid multiple scattering but still extract correct particle motion information. To measure particles in concentrated suspension, three techniques have been developed, i.e., frequency analysis, photon cross correlation function, and back scattering. Using these techniques, particle size measurement in suspension up to concentration of 40% or higher can be realized. Among them, the back scattering arrangement has been proven being the best approach in effectively avoiding multiple scattering and maximizing signal strength.

However, in any case, even though multiple scattering can be avoided or filtered, particle-particle interaction always exists so particles' motions are not pure Brownian but affected or constrained by interaction. The affection of interaction to measured size cannot be simply predicted or calculated. Therefore, the size and its distribution yielded from measurement are only apparent and not the real hydrodynamic size.

For measuring subnanometer particles or molecules, because of their fast motion and weak scattering, an instrument has to have a high power light source and a detector with fast photoelectron response and high sensitivity. Small and rugged coherent laser diodes having high powers with low costs have mostly replaced traditional He-Ne laser as the industrial standard for DLS instrumentation. Even though some avalanche photodiodes now can be used in DLS, for strict photon counting, thanks to advancement and reduced cost in photoelectron detectors, high grade photomultiplier tube is still a better choice. In addition, a different type of correlator that correlates photon arrival time interval instead of time domain photon counting often has to be used in situations when during a sampling time there are few or no photons. For example, if the photon count rate is 10^6/sec, at a sampling time of 50 ns, there will be in average 0.05 photons. In this instance, photo counting will be inefficient and a time-of-arrival correlation has to be used in obtaining a good autocorrelation function. With the combination of high sensitive photo detector, efficient and precision optics and fast time-of-arrival correlator, size measurement of fullerene molecules or even thiamin molecules (Mw=337 Dalton) can be achieved.

2 ZETA POTENTIAL DETERMINATION

For small particles in liquid, there is no satisfactory technique to determine surface charge of particles. The common practice is to determine electric potential of a particle at a location away from the particle surface, somewhere in the diffuse layer. This location, related to

particle movement in liquid, is called slipping plane or shear plane. The potential measured at this plane is called zeta potential. Zeta potential is a very important parameter to colloidal or nanoparticles in suspension. Its value is closely related to suspension stability and particle surface morphology, therefore it is widely used in product stability study and surface adsorption research.

In zeta potential determination of suspended particles, even though there exist three types of technologies, i.e., electrophoretic light scattering method, acoustic methods and electroacoustic method, due to its measurement sensitivity, accuracy, and versatility, electrophoretic light scattering is by far the best technique that has been widely used in many applications [2]. However, classical electrophoretic light scattering using a small scattering angle typically between 8 to 30 degrees cannot be used for concentrated samples. Since zeta potential, unlike particle size or molecular weight, not only is the property of particles but also the environment surrounding particles, e.g., pH, ionic strength and even the type of ions in the suspension. Therefore, in many instances, even though zeta potential of suspended particles is measured after diluted by, typically, DI water and high resolution and accurate result is produced, the value has little or even opposite relation with the true value in the original environment. Therefore, the measured value may have no practical usefulness or sometimes even misleads the user.

To measure zeta potential distribution in concentrated suspension is a technological challenge. Acoustic methods only yield average value with low sensitivity provided that the solid concentration is known. The back scattering approach used in size measurement cannot be adopted due to interference of Brownian motion to oriented electrophoretic motion at large scattering angles. For example, for a 250 nm particle with zeta potential of 60 mV, when it is subjected to a 30 V field, the electrophoretic motion will produce a Doppler shift of 55 Hz at a scattering angle of 10 degrees and the Brownian motion of the particle will cause a 3.5 Hz peak broadening. If the measurement is performed at a scattering angle of 160 degrees, the Doppler shift and peak broadening will be 108 Hz and 430 Hz, respectively, making accurate determination of zeta potential impossible.

Lately, a unique optical arrangement for measuring zeta potential in concentrated suspension has been invented [3]. In this invention, a unique electrode that is conductive but transparent to both illuminating and scattering lights is used in electrophoretic light scattering measurement. The incident light entering from one side of a thick window is refracted by the window and exits the window to the sample cell through a surface, which is perpendicular to the first surface, on which a thin metal coating serves as the transparent electrode. Particles are moving electrophoretically in the field created by this electrode and another ordinary electrode. Light scattered from particles near the window surface are refracted twice before exiting from the other side of the window. This configuration enables a similar arrangement as in back scattering PCS but at a much smaller scattering angle (~30 degrees). The additional advantage of this technique is that because of the scattering volume location, there is no electroosmotic flow typically caused by surface charge of cell side walls. Therefore, the Doppler shift measured is only from particles motion without interference from liquid motion. Particle size measurement in concentrated samples can also be performed using this sample cell when electric field is not applied.

This invention has been utilized in an instrument (Delsa^{TM}Nano from Beckman Coulter, Inc.), which is capable of performing nanoparticle size measurement using forward scattering and back scattering PCS at multiple scattering angles and zeta potential measurement for nanoparticles in either low concentration or turbid samples, in addition to its capability of measuring zeta potential of solid surface or film. Nanoparticles or molecules in various concentrations can be characterized with the combination of precision optics, high sensitive and fast response photo detector, and the transparent electrode technology. For example, particle size increment from 2.8 nm to 6.2 nm and zeta potential increment from 7.2 mV to 7.6 mV when the generation of dendrimers increased from 3 to 5 have been successfully captured.

3 COUNCLUSION

Ensemble particle characterization techniques that characterize particulate systems, not a few single particles, will continue to play a very important role in nanotechnology, especially when more and more nonmaterial are being transformed from academic and laboratory research to production of different scales. In quality control environment, sample analysis often has to be performed quickly and easily without complicated sample preparation procedure and with minimum alteration to the sample. The technologies introduced in this article, i.e., back scattering and electrophoretic motion detection through a transparent electrode, can meet such demands: both particle size and zeta potential measurements can be performed in concentrated suspension without dilution. On the other hand, with particle dimension decreasing to a few nanometers or smaller, requirements for high sensitivity and fast photoelectric response become important for any light scattering instrument.

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