

Application of Atomic Force Microscopy on Particle Characterization

Application Note

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Introduction

Particles, especially nanoparticles are of great scientific interest because their properties change as the size approaches the nanoscale. The properties include optical, magnetical, mechanical, electronic and thermal property etc. Due to this unique feature, nanoparticles not only attract much attention from the scientific community but also are becoming more and more important in practical applications such as coatings, data storage, catalyst and nanoelectronics. Nanoparticle characterization is a key step

to understand nanoparticle's properties and to control the manufacturing and applications. Normally nanoparticle characterization especially sizing, is done by a variety of methods such as light scatter methods, sedimentation methods, electrical property method and imaging methods. Except the imaging method, all methods measure particle sizes indirectly, since the size is interpreted based on a model or a theory from some measured parameters. Among the imaging techniques, optical microscopy, electron microscopy and scanning probe

microscopy are the main techniques. Optical microscopy can only be applied to measure particles with a size larger than one micron. Electron microscopy can measure particles down to nanometer size in vacuum conditions, while the sample preparation is complicated.

Scanning probe microscopy, mainly atomic force microscopy (AFM) offers several advantages in particle characterization. It provides 3D information about particles size. It is capable to provide other information such as particle shape, surface area, electrical property, roughness and chemical composition in most cases. With the powerful data process software, AFM can also provide statistical parameters of particles such as the size distribution, area distribution, volume distribution. Moreover, AFM can characterize particles in different environment including air, vacuum, liquid, special gases, elevated temperature, low temperature etc. Compared to electron microscopy, sample preparation is easy. Samples can be conductor, semiconductor or insulator.

Capability of Measurement of Particle Sizes with High Spatial Resolution

AFM has a very high resolution (sub-Angstrom) for its measurements in Z direction. Therefore, even sub-1 nm particles can be measured accurately if they are positioned individually on a flat substrate such as mica, which is atomic-level smooth.

Figure 1 shows two samples of isolated nanoparticles imaged by AFM in AC mode. One is a cell lysate, which is an insulating biosample. The other is conductive gold collides. The colors on the images represents different height. For a detailed

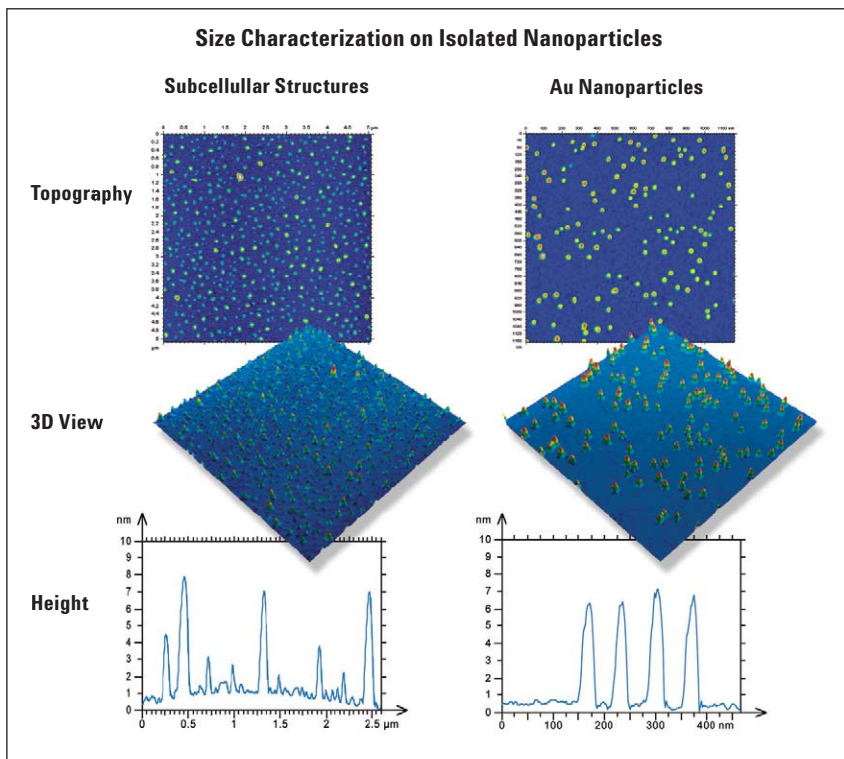


Figure 1. AFM height measurements on a biological nanoparticle sample (left) and an inorganic nanoparticle sample (right). The top row is the topographic images (5 µm x 5 µm left and 1.2 µm x 1.2 µm right) and the bottom row is the cursor profiles of the lines on the AFM images respectively.

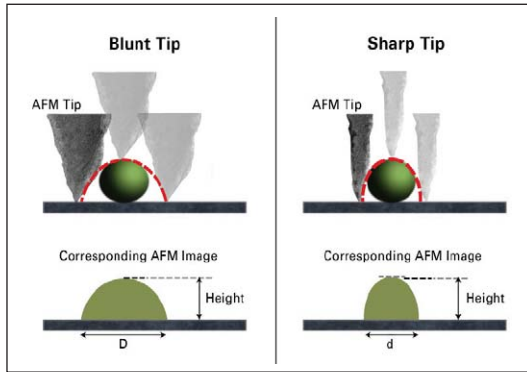


Figure 2. Schematic drawings illustrate tip convolution effect.

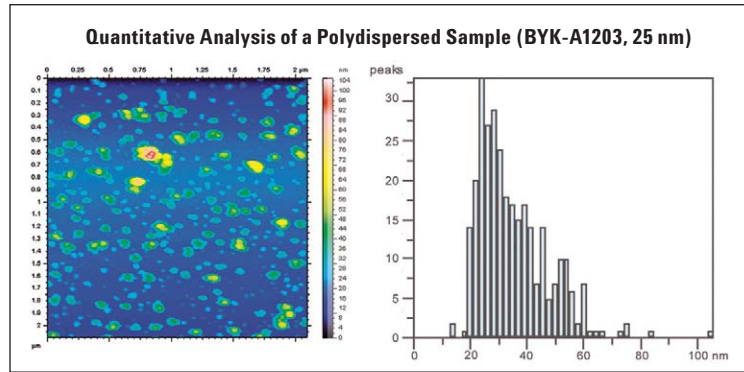


Figure 3. An AFM topographic image of Al_2O_3 on mica and its corresponding size distribution histogram (right) generated by Pico Image. Scan size $2.1\mu\text{m} \times 2.1\mu\text{m}$.

and quantitative analysis, a cursor profile can be extracted from the data. We can clearly see that the lysate particles having height ranging from 2 nm to 6 nm. For gold nanoparticle on silicon wafer, the cursor profile showed that the particles are uniform, with a height of 6 nm.

In addition to the accurate measurement on Z direction, AFM also delivers a high resolution and accuracy in XY directions. Yet for isolated particles, it is more accurate to probe their sizes based on the height than the lateral measurement. Intrinsicly, AFM image is a combination of the tip geometry and the sample geometry. Figure 2 illustrates this tip-convolution effect. Clearly, the lateral size of a tip is sharpness dependent. A blunt tip results in a larger lateral size, and a sharp tip gives a lateral size close to the real one, while the height of the particle remains the same in both situations.

While AFM provides the high-resolution measurement at single particle level, ensemble processing or statistical data analysis can be achieved using powerful particle analysis tools such as the Agilent AFM data processing software Pico Image. For example, statistical information such as particle counting, mean particle size and particle size distribution can be achieved quickly. Particle sorting by criteria such as area, equivalent diameter, orientation, aspect ratio, roundness is also available.

Figure 3 shows an AFM topographic image of a sample Al_2O_3 . By using the data process function "peak count histogram", we can get the quantitative height distribution of all the particles within this specific image. We can also export the histogram as a data file. In the case that multiple images were taken at different locations of the same sample, this

function allows users to combine all the data files and get a more representative particle size distribution histogram based on a larger ensemble.

Capability of Measurement of Particle Sizes with Wide Range

Most of commercial AFM instruments have a larger scan range in lateral directions than the vertical one. For example, the large Agilent AFM scanner typically offers a $80\mu\text{m}$ by $80\mu\text{m}$ lateral size in XY directions and a corresponding $5.5\mu\text{m}$ in Z axis. For very big particles especially those having a size larger than scanner Z range, size characterizations are still allowed from

AFM studies. In this case, particles should be prepared on the substrate in such ways that they are close-packed on the surface. For particles which can form a packed monolayer on the surface, particle size can be determined by measuring the distance between two neighboring particles, tip convolution does not interfere with the distance measurement on XY directions. Figure 4 shows several examples in which all the particles are closely packed. In this case, the size range that can be accurately measured depends on the lateral resolution of the AFM and the scanner's scan size. For a scanner with a scan size of $100\mu\text{m}$, the particle size range that can be measured is from $<1\text{nm}$ to $50\mu\text{m}$.

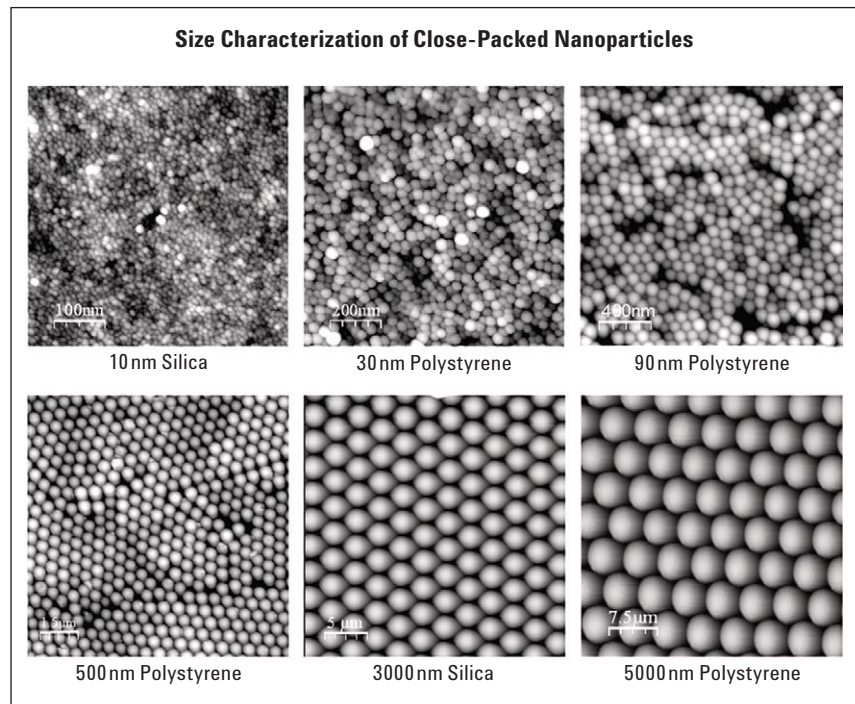


Figure 4. Topographic images of some closely packed particles with a diameter of 10 nm, 30 nm, 90 nm, $0.5\mu\text{m}$, $3\mu\text{m}$ and $5\mu\text{m}$, respectively.

Nanoparticle Shape Measurement

For the characterization of particles, particle shape analysis is becoming more and more important in addition to particle size. Varying the shape of the particles results changes in the surface area dramatically. Since the surface area determines how fast a chemical reaction occurs, particle shape is an important parameter in the pharmaceutical and chemical industries. The most commonly used technique for shape analysis is imaging technique. Optical microscopy and TEM provide images that are 2D projects. Although SEM is able to provide a 3D view of the sample, it is very difficult to get the true value on the vertical direction. AFM offers visualization on three dimensions with sub-nanometer resolution and precision. In Figure 5, a fiber like silicon nitride nanostructure and a rectangle shaped Yttrium Oxide is shown.

Capability of Material Differentiation

In addition to the unprecedented high spatial resolution, another key advantage of AFM is the simultaneous multi-channel data acquisition. In AC mode, tip-sample force interactions cause changes in amplitude, phase and the resonance frequency of the oscillating cantilever. The spatial variation of the change can be presented in height (topography) or interaction (amplitude or phase) images that can be collected simultaneously. Phase signal is very sensitive to the

mechanical (stiffness, friction) and adhesive properties of samples. Therefore, it provides a means to probe the materials composed in nanoparticles. Figure 6 shows the AFM imaging of a sample, that contains two types of polymer particles with different sizes and materials. One is poly (butyl methacrylate) with a mean size of 128 nm. The other is a copolymer (50% butyl acrylate\ 46% polystyrene\ 4% methacrylic acids) with a larger size of 217 nm. The mixing of both particles on surface has been verified because topographic images (Fig. 6A and 6C) clearly reveal the coexistence of the two types of particles with lateral dimensions corresponding to their characteristic sizes. The sample is imaged first under low force with a purpose of better visualization of the topography. Under such condition,

the difference in phase signals between two types of particles is negligible (Fig.6B) as the tip-sample interaction is not strong enough. With an increased imaging force, the material sensing is enhanced dramatically so many small particles exhibit a much brighter contrast with respect to the larger copolymer ones (Fig.6D). The observed phase contrast variation is due to the intrinsic natures of materials. The copolymer is softer than the PMA (The Tg of Poly(butyl methacrylate) is 30 °, while that for the copolymer is 20 °C). Therefore, phase imaging distinguishes the types of materials due to the different hardness.

Shown in Figure 7 is another example to further demonstrate the AFM capability of material differentiation with higher spatial

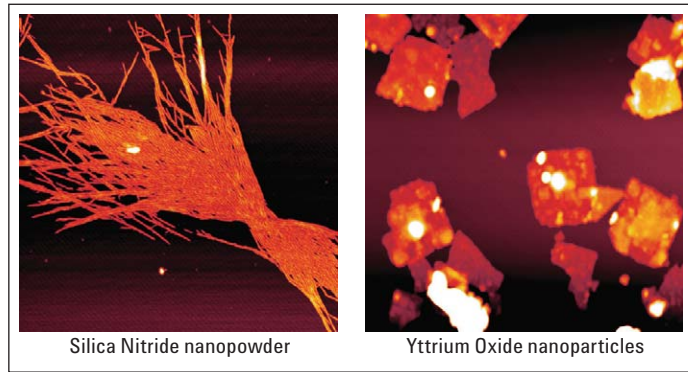


Figure 5. Topographic images of a SiN nanopowder, scan size 3.6 μm (left) and a Y_2O_3 nanoparticles, scan size 2 μm (right) on mica surface.

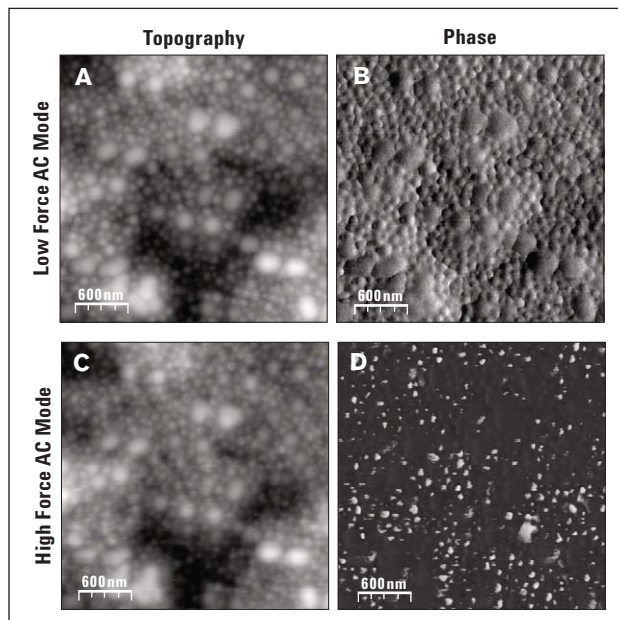


Figure 6. Topographic images (A,C) of mixed polymer nanoparticles and the corresponding phase images (B,D) at different image forces. Scan size 3 μm x 3 μm .

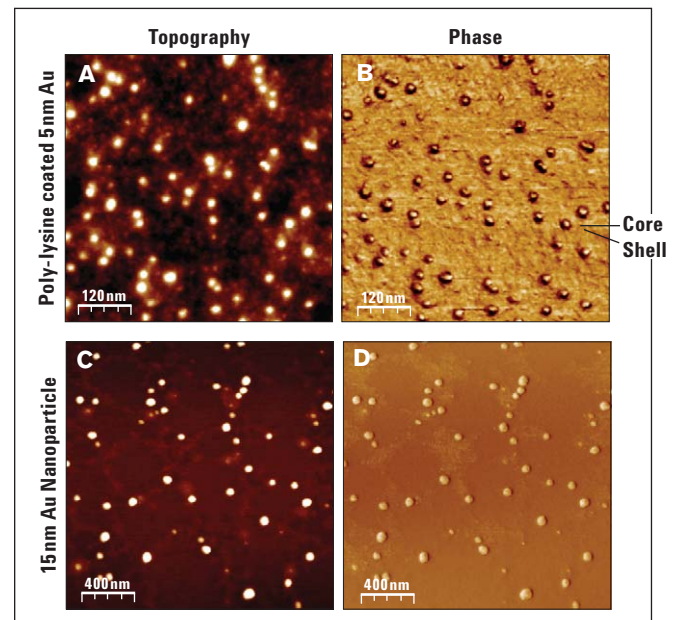


Figure 7. AFM topographic (A,C) and phase (B,D) images of poly-lysine coated 5 nm Au colloids (top, scan size 600 nm x 600 nm) and 15 nm Au nanoparticles (bottom, scan size 2 μm x 2 μm) on mica.

resolution. In this case, both conjugated and unconjugated gold nanoparticles smaller than 20 nm are studied. Figure 7A is a topographic image of 5 nm cationic colloidal gold modified with a poly-lysine coating. Since the organic layer is softer compared to the metal core part, the outer coating appears as dark ring in the corresponding phase image (Fig.7B). Figure 7C and D are topographic and phase image of unconjugated 15 nm Au nanoparticles from a blank experiment. As expected, the phase image does not show a different contrast at locations of particle edge. It confirms that the ring structures observed in Figure 7B are associated with the poly-lysine coating.

Conclusions

Atomic force microscopy is an indispensable technology for material characterization because of its versatility and unprecedented spatial resolution. For particle size analysis, AFM provides accurate measurement of particles ranging from 1 nm to 50 μm at single particle level. Meanwhile, statistic investigation of a large population of poly-disperse particles is allowed using particle analysis module in advanced software. AFM is also capable of material sensing, which offers to differentiate various types of particle or identify the heterogeneous components within the individual particle.

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