Atomic Force Microscopy: Is It Just an Imaging Technique?

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Atomic Force Microscopy (AFM), without any doubt can be named as one of the most sensitive imaging techniques which allows researchers to explore a broad spectrum of materials such as semiconductors, nanocrystals, biological materials, pharmaceuticals, polymers etc.[1] In recent years, AFM has demonstrated the ability of generating images with resolutions high enough to visualize sample features measured in fractions of nanometers or "atomic resolution". AFM uniquely offers unprecedented spatial resolution imaging owing to its high force sensing capability and nanometer scale position accuracy. Thus, AFM has gained a great interest across the disciplines having applications in chemistry, physics, material science, engineering and biology. Recently, it has also been utilized in the direct quantification of various properties of material such as electrical, mechanical, dimensional, magnetic, electrochemical, surface tension, protein folding and binding interactions.[2,3]

AFM was first invented in 1986 by Gerd Binnig, Calvin Quate and Christoph Gerber to overcome the limitations of its ancestor, scanning tunnelling microscopy (STM).[4] STM utilizes a sharp metal tip which is raster scanned over the surface to obtain an image and has the ability to reach atomic level resolution. Hence, it led to a great encroachment in science over the other microscopic techniques such as light or electron microscopy. Even though STM was a versatile tool, it suffered from limitations where atomic level resolution could only be attained with conducting samples under vacuum and controlled conditions. Further, STM was not capable of monitoring the force experienced by the samples. Hence, to overcome these limitations, AFM, which has the capability to achieve atomic level resolution even with nonconductive samples was developed. AFM can be operated under ambient conditions in air and liquid medium while measuring forces with a piconewton (pN) sensitivity. AFM also has the advantage where a wide variety of samples including soft materials such as cells and flexible polymers, hard materials such as ceramics or metal particles, conductive or nonconductive material can be imaged. Furthermore, in recent years, AFM has been utilized to obtain images of even single atoms or molecules within a chemical structure.

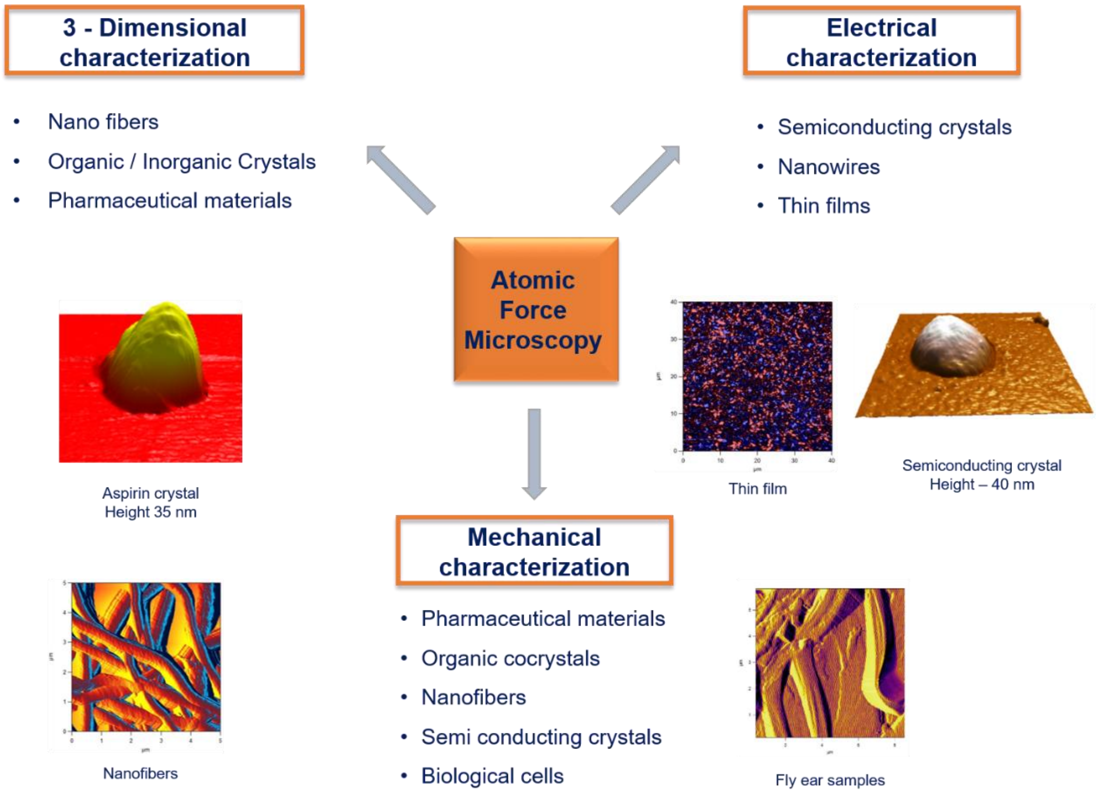

Figure 1. Few applications of Atomic Force Microscopy in Chemistry, Biology and Material Science[1]

The first ever atomically resolved image collected using force spectroscopy was reported in 1995 for a Si (111) -7x7 surface.[5] Since then, there have been many major breakthroughs in developing new quantitative AFM based imaging techniques, enabling scientists to visualize and map spatial arrangement of chemical groups on a wide variety of materials including organic materials, biological cells and inorganic compounds. Furthermore, AFMs have produced desktop-worthy close-ups of atom-sized structures, ranging from single strands of DNA to individual hydrogen bonds between molecules, in the recent history. Such detailed images of atom-sized structures led to new advents in many scientific fields such as biology, material science and chemistry.[5] However, collecting these

[1] Images collected by T. Rupasinghe, University of Iowa, USA

high resolution AFM images was a meticulous and time-consuming process. Therefore, until about 2005, AFM was mostly used to image static samples which do not undergo any changes during the capture. In 2015, a group of Massachusetts Institute of Technology (MIT) scientists made a foremost discovery by introducing a high-speed AFM which scans 2000 times faster than an existing AFM, and capable of even collecting pictures of chemical processes taking place at nanoscale.[6] Furthermore, the sensitivity and the speed of this newly introduced AFM enabled the scientists to see atomic scale processes such as dissolution, nucleation, condensation, deposition of materials, which were never observed before in real-time. Moreover, with all these advancements, today AFM has become a versatile imaging technique which opened many new advents in science, especially at the nanoscale.

Apart from its use as an ingenious imaging tool, AFM has different spectroscopic modes which measures electrical, mechanical and magnetic properties of materials at nanoscale which is of enormous important in understanding structure-property relationships. Establishing reliable structure-property relationships of materials is essential for the potential design of novel materials with tunable mechanical, electronic, optical, and chemical properties. For example, in organic solids, understanding of physical and intermolecular phenomenon in the context of crystal engineering and thereby, establishing relationships between structure and electrical properties is essential in order to design novel organic solids with improved electrical properties. This type of understanding can further be tailored into molecular level device fabrication, material science applications and other applications in molecular electronics. Furthermore, in pharmaceutical industry, establishing reliable structure - property relationships are important in achieving active pharmaceutical ingredients (APIs) with better tabletability, improved pharmaco-kinetic properties, and higher stability.

However, a key challenge in understanding properties of nanomaterials is the limitation of available techniques that can be used to measure such properties. Due to size constraints, traditional methods in measuring electrical properties of materials cannot be applied in the nanoscale. However, in recent years, AFM has successfully faced this challenge and it has been utilized to quantify electrical and mechanical properties of novel nanomaterials such as organic-inorganic hybrids, graphene sheets, cocrystals, nanocrystals, thin films, etc.[2,3]

Electrical Characterization of Materials using AFM

One of the unique applications of AFM is its ability to measure electrical properties of nanoscale materials with high accuracy. As traditional methods in measuring electrical properties of materials cannot be applied in the nanoscale due to size constraints, AFM based electrical characterization is of enormous importance as it has the capability to visualize different features of nanomaterials while measuring electrical properties.[2]

The specific technique which measures electrical properties using AFM is conductive probe AFM (CP-AFM). Recently, this has extensively been used in the electrical characterization of nanowires, thin films or monolayers, nanocrystals, graphene sheets, etc. CP-AFM has the unique ability to measure force, current, and bias, simultaneously and independently and it allows the direct quantification of electrical properties. Briefly, in CP-AFM, a sharp conductive probe is used to electrically connect to nanostructures on a conductive substrate. Then a voltage is applied between two electrodes (conductive probe and the substrate) and resulting current is recorded as a function of applied voltage. Resistance of the sample is calculated using Ohm's law and converted into resistivity or conductivity.[2] Importantly, CP-AFM has the ability to measure local electrical properties and at the same time imaging is not limited to conductive samples like with STM.

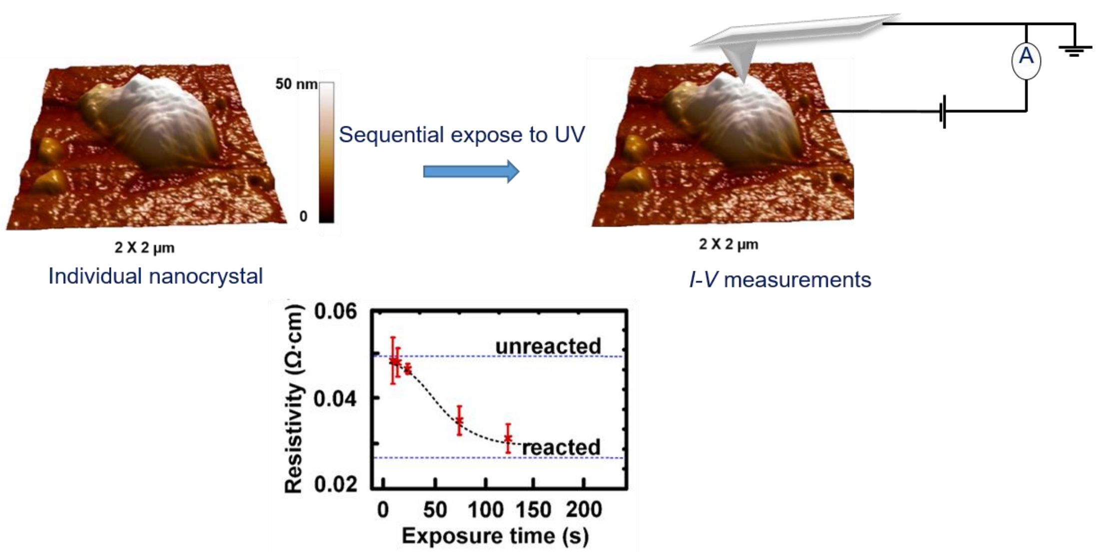

Figure 2: Example of an in-situ CP-AFM experiment, measuring conductivity of a nanocrystal undergoing a photoreaction in real time.

Mechanical Characterization of Nanomaterials using AFM

Another important application of AFM is its unique capability to measure mechanical properties of nanoscale materials. As mentioned before, size constraints limit the use of traditional methods in quantifying properties at the nanoscale. AFM based nanoindentation technique has been used in the mechanical characterization of nanocrystals, thin films, semiconductors, nanowires, polymers, biological materials, pharmaceutical crystals etc. This technique allows direct quantification of mechanical properties of small volume materials in the form of Young's moduli with high accuracy.[3]

Specifically, the AFM tip is used to indent a sample of interest and force *vs* displacement curves are collected while indentation takes place and the Young's modulus of the sample is calculated using well-known Hertzian contact model.[3] Compared to other depth sensing instruments, AFM is advantageous as it allows us to relate the morphology (obtained from high resolution imaging capability of AFM) to local mechanical properties, which is not possible with other instruments.

Applications of AFM in Biology

Apart from the above applications, today AFM has become an emerging tool in the field of biology where AFM is used to quantifying various properties of biological materials. Furthermore, AFM has taken a front seat in driving new developments of nanobiotechnology and due to the unique features of AFM there is now ever-increasing emphasis on applying nanoscale forces to investigate biological events. Herein, AFM's unique ability of operating in several environments, including vacuum, air and most importantly the liquid environment, in which most of the biological processes take place, is of paramount important. In addition to the visualization of biological materials such as single cells, single protein and DNA strands in their active environment, AFM is capable of single-molecule manipulations through molecular recognition force spectroscopy, exploring cellular mechanics and biological mechanisms and enzyme-drug interactions[7].

Over all, it can be emphasised that, although AFM is often considered as an imaging tool which provides atomic-scale resolution, it offers many other unique features which can be utilized in exploring new advents in many field such as biology, chemistry, medicine, nanoscience and material science.

Guest article published in Chemistry in Sri Lanka, Published by the Institute of Chemistry, January 2019, Vol 36, No 1

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