Standardization of Nanomaterials Characterization by Scanning Probe Microscopy for Societal Acceptance

Daisuke Fujita¹, Keiko Onishi² and Mingsheng Xu³

¹ International Center for Materials Nanoarchitectonics (MANA) and Advanced Nano Characterization Center (ANCC), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
² Advanced Nano Characterization Center (ANCC), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
³ International Center for Young Scientists-Interdisciplinary Materials Research (ICY-S-IMAT), National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

E-mail: fujita.daisuke@nims.go.jp

Abstract. Novel nanomaterials are expected to play key roles for the promotion of innovations in the various industrial products. In order to make such novel nanomaterials to be socially acceptable and widely used, it is very important and necessary to establish the reliable nano-characterization methodology for the industrial nanomaterials under the authorized international scheme for standardization. Among the nano-characterization methods, scanning probe microscopy (SPM) is the most versatile both in the measurement functions and the operational environments. Whereas there are various nanomaterials of industrial application, fullerene nanomaterials (FNM) have attracted much attention due to their unique physical properties. Here we show the importance of the quantitative analysis and standardization of SPM using FNM as a typical example.

1. Introduction
Nanomaterials can be defined as engineered structures with at least one dimension of approximately 100 nanometers or less [1]. Since the functional nanomaterials are expected to play key roles for the promotion of innovations in the various industrial fields, these nanomaterials have been increasingly employed for the commercial purposes during this decade. With the increase of the engineered nanomaterials circulated in the society, the potential impact and risk on the environment and the health of human being have attracted a growing attention in the world [2]. Especially the potential cytotoxicity of nanoscale carbon materials such as single-wall nanotube (SWNT), multi-wall nanotube (MWNT), and fullerene-based nanomaterials has been a matter of interests among the so-called nano-toxicologists [3, 4]. There has been a problem in the quantitative evaluation of nanoscale toxicity and conflicting results on the biological effects of carbon nanomaterials have been reported, in which
some reports high and others low toxicity. The observed discrepancy is mainly caused by the
distribution of size and the impurity concentration such as the metal catalyst and the surfactants used
for solubilization. Therefore, the establishment of quantitative characterization methodology at the
nanoscale is now considered to be pre-requisite for the reliable risk assessment.

On the contrary, in order to trade the engineered nanomaterials globally, it is also required to
specify the properties of the nanomaterials using the unified terminology, nomenclatures, definitions,
and measurement methodology. Especially, how to measure the basic properties at the nanoscale, such
as dimensions, size distribution, atomic structure, chirality, impurity content, electrical conductivity,
magnetic property, specific surface area, and so on, shall be important items to be specified in a
unified manner. Thus, in order to make the novel nanomaterials be socially acceptable and be
smoothly traded in the world, it is important to establish the reliable nanocharacterization
methodology under the authorized international scheme for standardization [5,6].

Among the nanoscale characterization methods, scanning probe microscopy (SPM) can probe the
most powerful and versatile method. Top two of the various important innovations in the SPM
development are the inventions of scanning tunneling microscopy (STM) and atomic force microscopy
(AFM), which were invented in 1982 and 1986, respectively [7,8]. Since then, various kinds of SPM
have been developed, which enables us to probe a variety of physical and chemical quantities. Owing
to the compactness, SPM has a high environmental adaptability. SPM can be operated not only in air
but also in liquid and in ultrahigh vacuum. Furthermore, SPM probes can be used as versatile tools for
nanoscale fabrication and atom manipulation [9]. Nowadays, SPM is used not only for basic research
but also for fabrication and inspection processes in industry.

In this perspective article, the recent activities and researches related to the standardization of
nanotechnologies and SPM standardization is described firstly. These activities are performed in two
technical committees (TC229 and TC201) of the International Organization for Standardization (ISO).
Next, current challenges in the SPM standardization on quantitative analyses are discussed based on
the ISO/TC201 activities [10]. Besides the quantitative reduction methodology of morphological
artifacts caused by the finite size of SPM tips is introduced [11,12]. Finally, actual applications of the
AFM image restoration methodology to the actual nanomaterials are explained.

Here, among various nano objects, fullerene nanomaterials (FNM) are focused since they have
attracted much attention due to their unique physical properties. Especially low-dimensional fullerene
nano-crystals such as fullerene nanowhiskers (FNW) and nanotubes (FNT) are attractive since they
exhibit semiconducting transport property. Actually the electric property of FNWs has been clarified
by using a conductive AFM method [13]. Such low-dimensional semiconductor FNMs may represent
promising building blocks for the bottom-up assembly of integrated electronic and photonic systems.
Obviously the most significant role of AFM is the precise evaluation of the dimensions of
nanostructures. Effectiveness of the image restoration methodology for distorted AFM images using
an actual tip shape function is demonstrated.

2. International Standardization in Nanotechnologies

A brief history of the international standardization in the area of nanotechnology is schematically
shown in Fig.1. The first initiative for pre-standardization research on nanotechnologies within an
international collaboration scheme was thought to be the establishment of a new technical working
area (TWA29) on “materials properties at the nanoscale” of VAMAS (Versailles Project on Advanced
Materials and Standards) in 2002. VAMAS supports world trade in products dependent on advanced
materials technologies, through international collaborative projects aimed at providing the technical
basis for harmonized measurements, testing, specifications, and standards [14]. Recently VAMAS has
approved to establish another new technical working area (TWA34) on “nanoparticle populations”,
which will first deal with refining the measurement of chirality distribution in polydisperse SWNT
sample. The main mission of VAMAS activity is to promote the international collaborative research
on pre-standardization through the international round robin tests. The final technical reports shall be
transferred to the corresponding ISO or IEC (International Electrotechnical Commission) committees for the detailed refinement towards international standards.

Actual standardization initiative in comprehensive nanotechnologies was first started in Europe, where CEN (European Committee for Standardization) established BTWG-166 on nanotechnology in 2004. CEN/BTWG-166 has been succeeded by the establishment of CEN/TC352 on “Nanotechnologies” at the end of 2005. During the same period, the American National Standard Institute (ANSI) launched Nanotechnology Standard Panel (ANSI-NSP) in 2004, serving as the cross-sector coordinating body for the purposes of facilitating the development of standards in the area of nanotechnology. Soon after ASTM International Committee E56 (ASTM-E56) on nanotechnology was formed in 2005. In Japan, Japanese Standard Association (JSA) formed Nanotechnology Standardization Panel in 2004, which was followed by the establishment of Japanese Nanotechnology Standardization Committee by JISC (Japan Industry Standards Committee) in 2005.

The proposal of a new technical committee (TC) dealing with the standardization of nanotechnologies on an extensive scale was done by British Standard Institution (BSI) in 2004 within the framework of ISO, which resulted in the establishment of ISO/TC 229 on “Nanotechnologies” in 2005. A year later, another technical committee dealing with electrical aspect of nanotechnology was set up in IEC as TC113. The purpose of the IEC TC113 is to deal with the relevant nanotechnological aspects in developing generic standards for electrical products and systems. Among the above activities of standardization in nanotechnologies, the scheme of ISO/TC229 is thought to be the most world-wide, since it has made liaisons with the related activities for standardization or pre-standardization of nanotechnology. TC229 has first established three working groups (WGs) such as JWG1 (terminology and nomenclature), JWG2 (measurement and characterization) and WG3 (health, safety and environment), in which two are joint working groups with IEC TC113. As for the measurement and characterization, the standardization of measurement methodologies for carbon nanomaterials such as SWNT, MWNT and fullerene have been selected as highly prioritized working items in JWG2.

3. International Standardization of Scanning Probe Microscopy
The standardization activities on SPM were formed in the ISO framework in 2004 when Subcommittee 9 for SPM was established in TC201 for surface chemical analysis [10]. The most prioritized task was to standardize the terminology of SPM, because it will provide a firm basis for the following standardizations. It includes acronyms for SPM-specific terms, definitions and terms for

Fig.1. A rough view of international standardization activities related to nanotechnology.

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SPM methods, and acronyms and terms for contact mechanics. The following standardization on SPM shall proceed towards the standardization of data management and treatment, dimensional calibration, reference materials, and guidelines for operational procedures. The priority of the standardization is generally based on the actual needs of SPM users, manufacturers and vendors. Since SPM has a large versatility in functions and applications, the standardization should deal with not only quantification of dimensional analyses by topographic imaging but also atomic-scale chemical analyses, fabrication and manipulation techniques, electric and magnetic property analysis, nanomechanical property analysis and so on. Moreover, guidelines for the proper uses of SPMs in different environments such as in air, in liquids, in UHV, and so on, should be standardized.

The major functions of SPM as analytical methods are imaging and spectroscopy at the nanoscale. The acquired raw data may require appropriate data managements and treatments. While a wide variety of SPM instruments have been manufactured since the invention of STM, a wide variety of data formats using different terminologies have been created by the SPM manufacturers. This situation may cause inconveniences for the SPM users to exchange data collected with different SPM instruments. The development of a standard data format shall facilitate inter-exchangeability and consistent treatment of SPM data, enhance the productivity of data processing programs, and increase accuracy and quantification. The proposed format consists of an information header and subsequent data array. Since the current data transfer format for surface chemical analysis (ISO 14976) is composed of text [15], the proposed data format for SPM is written in text format. The obvious advantage is that the data file can be accessed, independent of computer system, using text editor. The proposed arrangement of data array and the examples SPM data taken by different SPM instruments are shown in Fig.2. Once transferred to the standard format, it is easy to compare the individual data using the unified treatments.

Fig.2. (a) Geometry and arrangement for a two-dimensional map data array. (b)-(e) SPM images taken by different instruments and expressed by the data transfer format.

4. Quantitative Morphology Imaging of Nanomaterials

For quantitative morphology imaging of nanomaterials, it should be noted that significant distortion in imaging may occur if the sample surface has large corrugation compared to the tip apex shape [16]. The real surface topography, \( s(x,y) \), is dilated to the image surface topography, \( z(x,y) \), by the finite tip shape, \( t(x,y) \):

\[
z(x, y) = \max \{ s(x', y') - t(x'-x, y'-y) \}
\]  (1)
The dilated topography image can be partially restored by using the erosion algorithm to reconstruct the upper bound image, \(r(x,y)\), of the real surface topography:

\[
r(x, y) = \min\{z(x', y') + t(x'-x, y'-y)\}
\]

A numerical simulation of scanning (dilation) and reconstruction (erosion) of AFM topography imaging using a known tip-shape function is shown in Fig.3. Since there is a great need for a reproducible procedure for restoring AFM images, one should be standardized by the ISO.

For the engineered nanomaterials, one of the first prioritized properties to be specified quantitatively is their dimensions such as length, height, width, diameter, and so on. In order to realize the nanomaterials to be accepted as industrial products by market, it is necessary to establish quantitative methodology for critical dimension (CD) measurements using a noncontact mode AFM topography imaging. As for one-dimensional nano-objects such as FNWs, precise CD measurements of height, length and width are required, if they are to be traded in market. Typical crystal structure and outer shape of FNW is shown in Fig.4(a), which is likely to have a hexagonal cross-section. Compared with the raw AFM image shown in Fig.4(b), the reconstructed image using the tip shape function shows a significant reduction in width and sharpens the image as shown in Fig.4(c). The observed ratio of width/diameter is found to be consistent with the typical model structure shown in Fig.4 (a). However, it should be noted that the morphology of individual FNWs can be different.
In order to apply the image reconstruction in a quantitative and reproducible manner, it is critical to evaluate the tip shape function in use as precisely as possible using novel tip characterizers [17]. Since the quantitative CD measurement procedure of artificial nanoparticles at about 1 nm resolution should have potential industrial demands, pre-standardization research shall be performed.

5. Conclusion
In this perspective paper, we described the importance of international standardization of nanotechnologies and nanomaterials in order to make nanotechnology products be acceptable to the society and market. We pointed out that the precise and quantitative characterization of nanomaterials is prerequisite not only for fair evaluation of potential risk or toxicity of novel nanomaterials, but also for global trading of engineered nanomaterials or nano-products. Based on the strong demands for the nanotechnology standardization and pre-standardization research, various activities have been initiated in EU, US and Japan since 2002. After the establishment of ISO/TC229 on nanotechnologies, global standardization of nanotechnologies can be performed and discussed intensively since 2005.

Here we show the importance of the quantitative analysis and standardization of SPM using FNM as a typical example. Restoration of a dilated AFM topography image of FNW is successfully demonstrated. Since SPM can be used for the measurements of various materials properties, we have to promote the pre-standardization research for the versatility of SPM nanocharacterization.

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