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Characterization of nanoparticles as candidate reference materials

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Abstract: We report the characterization of three different nanoparticles (silica, silver and multi-walled carbon nanotubes) as candidate reference material. We focus our analysis on the size distribution of those particles as measured by different microscopy techniques.

Keywords: nanoparticles; reference material; nanometrology; size distribution.

1. INTRODUCTION

There is a growing number of reports about the new commercial products that have incorporated nanoparticles in their fabrication and which promise incredible new properties. Nanoparticles (NP) are, by definition[1], any object with all three external dimensions in the nanoscale[1], that is, between 1 nm and 100 nm. This definition, broad as it is, reflects the wide variety of applications of NPs, ranging from chemistry to biology, involving engineering, energy, fabrics and cosmetics.

Although NPs are already in use, there is still a gap in the regulation field, since technologies evolve faster than the norms. One of the main issues of the normalization process is the standardization of measurements methods of the particles and the production of reference materials (RM). All the main National Metrology Institutes are concerned with both the development of new NP RM and the establishment of standard methods for the measurements of NPs properties. Inmetro has also put considerable effort into this subject.

In the last few years Inmetro has participated in many interlaboratorial comparisons related to the measurement of nanoparticles such as carbon nanotubes, fullerene nanofibers, silica dioxide, silver and gold NP, among others. Those comparisons are held in the scope of international organizations such as VAMAS and Nanovalid. The former is a pre-standardization forum that organizes international collaborative projects aimed at providing the technical basis for drafting codes of practice and specifications for advanced materials[2]. The latter is a wide project whose main objective is the development of new reference methods and certified reference materials, including methods for characterization, detection/quantification, dispersion control and labeling, as well as hazard identification, exposure and risk assessment of engineered nanomaterials[3].

We present in this paper the main results obtained in the characterization of some of those nanoparticles and discuss the properties that make the studied particles good candidates for reference materials.

[1] Sometimes the term **nanoparticle** is also used to nano-objects with one dimension not in the nanoscale, like carbon nanotubes.

2. MATERIALS AND METHODS

2.1. Classes of particles

Three different nanoparticles have been characterized by different techniques: silica NP (SiO_2), silver NP (Ag) and multi-walled carbon nanotubes (MWCNT). These particles are good representatives of three classes of NP, as described below:

a) Silicon dioxide (silica): The NPs are typically spherical in shape, have a symmetrical size distribution and are very stable.

b) Silver: Unlike the oxide NPs, metallic NPs are less chemically stable; therefore they are usually produced as suspensions.

c) Multi-walled carbon nanotubes: The NPs have tubular shape with hardly controllable inner and outer diameters, as well as the number of walls. It is also a challenging task to obtain a good dispersion of nanotubes. Nevertheless, carbon nanotubes are already used in composite materials and biological applications, which makes important to have a CNT RM as a metrological tool for the evaluation and qualification of instruments and properties of materials containing CNT.

2.2. Dispersion

One of the main difficulties found in the characterization of NPs is the sample preparation, especially for microscopy. Since one measures individual particles, it is crucial to ensure good particle dispersion. On the other hand, the sample preparation process should not modify the particles' properties (structural, morphological). In the case of suspensions, it is important to guarantee that there is no interference from any additive in the solution as, for example, from stabilizing agents.

The dispersion of NPs is done, normally, using a solvent and ultrasonic bath to disperse the agglomerates. In some cases, this may not be sufficient and the use of ultrasonic probe and/or dispersion agents is necessary.

2.3. Techniques

Different techniques have been used in the characterization of physical and chemical properties of the NPs. Although microscopy (TEM, SEM and AFM) is the technique of choice for the dimensional characterization, other techniques such as BET, XPS, X-Ray diffraction and Raman, are also important. TEM analyses were performed with a FEI probe-corrected FEG Titan 80-300 microscope, operating at 300 kV. SEM images were acquired with a FEI Nova NanoLab 600 instrument, using 15kV acceleration. AFM measurements were done with a JPK NanoWizard instrument, operating in tapping mode at ambient conditions. BET measurements were done with a Quantachrome (Autosorb 1-C) instrument. The XPS analyses were performed in an ultra-high vacuum medium (pressure of 10^{-10} mbar) using an Al, Kα (hν=1486.7 eV) X-ray source, with power given by emission of 16 mA, at a voltage of 12.5 kV, in an Escaplus system from Omicron Nanotechnology. Wide-angle X-ray diffraction measurements have been carried out on a Bruker D8-Focus diffractometer in Bragg-Brentano reflection geometry using Cu Kα radiation (Ni-filter). Raman spectra were obtained with a RenishawInVia Reflex spectrometer, with an excitation laser of 514.5 nm (2.41 eV).

3. RESULTS

Microscopy (TEM, SEM and AFM) and XPS measurements were performed for all the samples. BET analyses were performed for silica and MWCNT, XDR for silver and silica, and RS only for MWCNT.

In general, all the NPs presented a high purity, as detected by XPS analysis. The size measurements with different microscopy techniques have also a good agreement, even with the great dispersion

of the results. Dimensional analysis of silver NPs could also be done with XRD. However due to the non-sphericity of the NPs, the comparison with the microscope results is affected. In the end of this section we compare the results obtained for each NP with the different techniques.

3.1. Silicon dioxide (silica)

XRD showed a broad peak centered at approximately 21° of 2θ, showing that the silica NPs were in amorphous phase. This information was also corroborated with RS. XPS analysis presented only peaks of silicon and oxygen, indicating the purity of the sample. BET analysis reported an average surface area of 886.20(35) m^2/g using N_2 and mean pore diameter of 4.0 nm as determined by BJH method.

Microscopy measurements report similar mean diameter sizes varying from 169 nm to 195 nm, but with a high standard deviation. Figure 1 shows an AFM image of NPs. These images were processed with SPIP 6.0.9 software measuring the height of 743 NPs.

The TEM measurements show that the NPs have a high sphericity but also broad distributions in diameter. Around 110 NPs were measured with TEM and SEM with manual processing.

3.2. Silver

Figure 2 presents SEM images of the silver NPs showing that the analyzed NPs had different shapes. The reported value is the calculated circle equivalent diameter (CED) which is the diameter of a circle with the same area as the 2D image of the particle. The same procedure was done in the analysis of TEM images. We see from the images that there is a high variation in the size of the particles (from 5 nm to over 100 nm) and it is also difficult to differentiate agglomerates from bigger NPs. Also the distribution is non-symmetrical so we report the median instead of the mean value of the distribution. Around 130 NPs have been counted in each technique.

In AFM measurements, 288 particles were analyzed avoiding the agglomerates and particles below 2 nm. The distribution is also highly asymmetric.

XRD diffraction pattern shows the peaks from Ag and also a broad background that can be related with the size distribution of the NPs. By modeling the shape of the NPs it is possible to extract the mean volume of the NPs and a volume equivalent diameter of around 17 nm. Once again, it is difficult to compare this result with microscopy results due to the very asymmetric

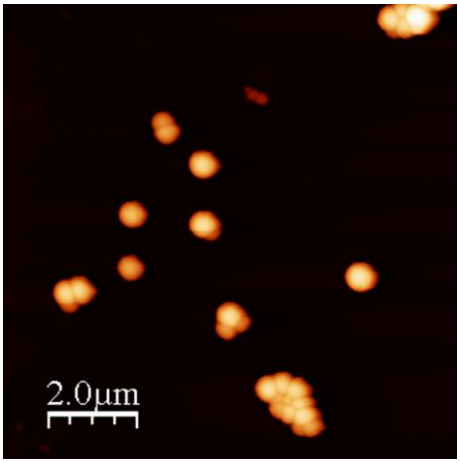

Figure 1 – AFM image of SiO_2 NPs.

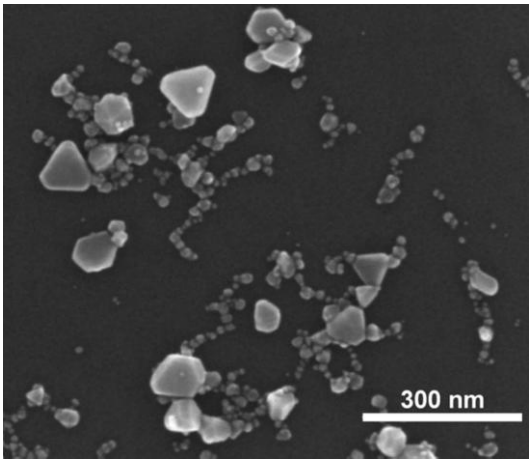

Figure 2 – SEM image of Ag NPs showing high variety in shape and size.

shape of the silver NPs.

XPS analysis showed that silver NPs were metallic (Ag^0 state) and also accused the presence of oxygen, nitrogen, carbon, sodium and sulphur. Those elements are probably from the residues of NP synthesis process.

3.3. Multi-walled carbon nanotubes

RS was performed in 5 different spots of the sample and we obtained an I_D/I_Gratio of 1.274(12). This shows that the sample is very homogenous and does not have many structural defects. This is corroborated by the TEM analysis. BET reported an average surface area of 264.2 m^2/g and XPS revealed essentially the presence of carbon and a very small contribution of oxygen, probably adsorbed in the sample.

TEM images (figure 3) show long tubes with different sizes of inner (2–12 nm) and outer (6–24 nm) diameters, but with regular interlayer distances of 0.351 nm. In general the tubes have a good structural shape with different degrees of cristallinity. It has also been observed some metal particles coming from the catalysts. AFM measurements presented a good agreement with the TEM results.

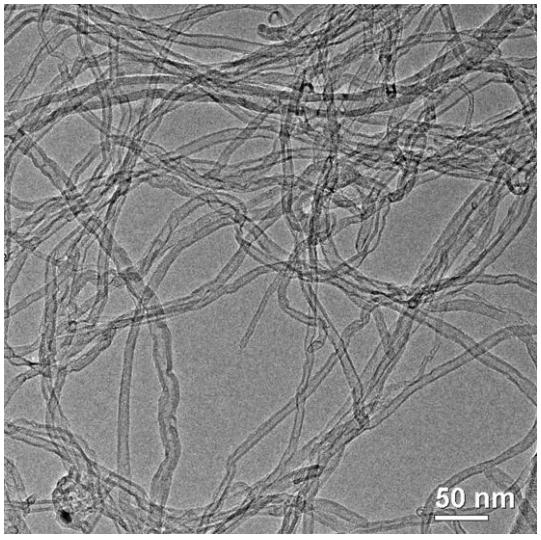

Figure 3 – TEM image of MWCNT with different diameters.

3.4 Size comparison

In the following table we compare the results of the size measurements of all the NPs with different techniques. We see that mean values, although of the same order, vary slightly within the different techniques. Also, the size distribution of the NPs is very large, what makes it difficult to find a better consensus between the measurements.

Table 1. Results of size measurement for the three nanoparticles with different techniques.

	Median and Standard deviation (nm)			
NP	**TEM**	**SEM**	**AFM**	**XRD**
Silica	169 (64)	158 (99)	195 (85)	--
Silver	13 (22)	19 (21)	11.4 (8.9)	17(1)
MWCNT	11.7 (4.7)	--	9.0 (3.0)	--

4. CONCLUSIONS

We have presented the characterization of three different NPs. We have seen that most of NPs have broad size distribution and the reported values from different techniques vary slightly, evidencing the need of find new materials to be our RM. It is clear that for the production of NPs RM is fundamental to have good control in the production of those NPs searching for a narrow size distribution that can allow a better comparison between results of different analytical techniques.

This preliminary study has also been useful in the creation of measurement protocols for different types of NPs using the aforementioned techniques that will be applied in the future characterization of NPs RM.

5. REFERENCES

[1] ISO/TS 27687:2008: Terminology and definitions for nano-objects – Nanoparticle, nanofibre and nanoplate.
[2] http://www.vamas.org
[3] http://www.nanovalid.eu