AFM characterization of small metallic nanoparticles

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In this work, we present a detailed method to observe small metallic nanoparticles (size below 5 nm) with standard AFM equipment for users with a basic experience in AFM. We show that the particles are well dispersed in a solution before deposition onto a substrate, it is possible to image them individually by means of AFM. The particle size can also be measured from the images, considering the particle height, while the width is largely distorted by the tip geometry. Although AFM observations cannot substitute HREM studies, they can be complementary as AFM allows observation of aggregation states, difficult to image by HREM, and the possibility of characterizing the size of the protecting shell.

1. INTRODUCTION

Nanoparticles (NPs) exhibit physical properties that are different from bulk materials and result largely dependent on their size and structure, mainly because of two reasons: (i) the size of these systems reaches the typical lengths of some phenomena, it is expected that the response of the system depends on the boundary conditions (which are no longer periodic, but determined by the particle size), and therefore, to be different from bulk material. (ii) Because of the large ratio of surface to volume atoms in NPs, the surface energy becomes important when compared with volume energy and therefore, the equilibrium situation for NPs can be different from that of bulk materials.

Thus, it is essential to get a good structural characterization of the NPs in order to understand their properties and the size effects. Nowadays, the most powerful technique to analyse those structures is the Transmission Electron Microscopy (TEM) [1]. In particular, High Resolution Electron Microscopy (HREM) provides accurate data about the size, shape and crystallography of the NP, which can not be achieved by any other technique [2, 3, 4]. However, HREM measurements are carried out in UHV and some structures can be modified during the measurement. In the case of small NP (size below 5 nm) which are usually unstable, the energetic electron beam can also promote precipitation or particle growing during the measurement. Furthermore, information about the aggregation state and dispersion features on different substrates cannot be obtained from TEM studies. At this stage, Scanning Probe Microscopy (SPM) can be very useful as they are generally non-invasive techniques, do not require elaborated sample preparation and measurements can be performed onto a large variety of substrates [5]. Obviously, SPM that give information mainly about the NP surface can not substitute a HREM analysis, but they can be complementary in order to check if the preparation and measurement processes modify the size of the nanoparticles. Another interesting possibility with the SPM is to observe directly the tendency of the NPs to aggregate, or form ensembles, when deposited on different substrates. Nevertheless, for both techniques it will be difficult to identify the knowledge of the aggregation state for the same nanoparticles in colloidal solution, because in both cases a drop of solution is dropped onto a substrate and then leaved for drying. Among different SPM techniques, Scanning Tunneling Microscopy (STM) provides the best resolution [6]. However, this technique is limited by the electrical properties of the sample, as it is necessary a good conductivity to reach tunnel current. The Atomic Force Microscopy (AFM) is one of the most widely used SPM for the observation of nanostructures, since this technique does not need specific sample preparation. Although as AFM allows observation of aggregation states, with size of tens of nanometers is well established [7]. [8], [9], [10], the observation of small NP (below 5 nm size) is not straightforward [11] because the size of the NPs is about the limit of the technique resolution. Furthermore, when the particles are dispersed in a solution, and must be deposited onto a substrate to image them, the interaction with the tip can move the NPs, giving rise to the so-called "sweeping" effect [12], [13]. In this case, it is necessary to carry on the analysis carefully and looking for the best conditions in order to obtain proper information about the particle size. AFM experts can achieve atomic resolution and they are able to manipulate single atoms [14]. However, AFM is becoming more and more an "experts technique" but a general tool used by people working on nanostructures. In this work, we present a detailed method to observe small nanoparticles with a standard AFM and discuss the information that can be obtained from the measurements that can be carried out by persons with a basic experience in AFM.

2. EXPERIMENTAL

2.1 Materials

Samples analysed were nanoparticles of Pd, Au and Ag with sizes in the 1 to 5 nm range, and capped with different chemical species. Palladium NPs were obtained by a redox-controlled size-selective method using tetraalkylammoniumsalts as surfactants [15]. In this work a solution of Pd(NO3)2 was used as palladium precursor in an excess of tetraethylammonium acetate. Gold NPs protected with tetraalkylammonium salts were obtained by the chemical reduction of the precursor salt (HAuCl4) using sodium borohydride as reducing agent in the presence of tetrocycloalumium bromide as surfactant (i). Thiol-derivatized gold and silver NPs were prepared by chemical synthesis following the Brust method [16]. Sodium borohydride was used as reducing agent and dodecylamine as the thiol linker molecule. More details about the preparation of those samples has been described elsewhere [2, 3, 17, 18].
2.2 Method
The observations on mica using tapping mode were carried out with a Standard Cervantes AFM microscope from Nanotec. AFM probes were rectangular SiN Olympus cantilevers with pyramidal tips and resonance frequency of 77 kHz.

The size of Pd and Au NPs were also measured by HREM microscopy in order to compare them with AFM results. Colloidal solutions of sample were dropped onto carbon coated copper grids. After drying, the samples were analysed in a Philips CM200 TEM microscope working at 200 kV. Particle size distribution histograms were obtained by analysing several pictures with an automatic image analyser.

2.2.1 Substrate and measurement conditions.
In order to observe the NPs with the AFM two conditions must be achieved. First, the roughness of the substrate must be about one order of magnitude below the particle size, that is, ~0.3 nm. The second is that the resolution of the measurement must be within the same order of magnitude.

![AFM Image of Pd nanoparticles protected by tetrabutylammonium salts onto mica substrate.](image)

Several substrates can be used for image the NPs, as mica, highly-oriented pyrolytic graphite (HOPG), quartz and others [6],[19]. Actually, the results of the measurements may depend on the substrate used because of substrate-NPs interactions. In this work a slide of commercial mica was used as substrate. It is easy to obtain large very plain surfaces in mica by cleavage. However, these surfaces degrade easily in a few days when working in air because of pollution deposition and air moisture. Thus, clean surfaces were obtained cleaning the slide immediately before sample deposition and measurements. To cleave clean surfaces, adhesive tape was fixed to the surface of the mica slide and subsequently was retired by a firm and straight movement.

The resolution of the measurement can be increased maximizing the signal to noise (S/N) ratio. The observation of NP was performed in the so-called “tapping mode” that measures the modification of the tip oscillation amplitude due to the tip-sample interactions. We worked at constant amplitude: the system moves the tip up and down to maintain constant the tip oscillation amplitude. The vertical movement required to satisfy this condition while scanning the sample reproduces its topography. The “contact mode” is forbidden when the NPs are not strongly fixed or embedded in the substrate, because the tip mass is several orders of magnitude larger than NPs, so the lateral force should move the particles along the surface [12],[13].

In order to determine the best imaging conditions we measured amplitude vs distance, obtaining the curve shown in Fig. 1(a). This curve represents the oscillation amplitude of the tip as a function of the tip-sample (in this case the tip-substrate) distance. Actually, the y axis does not represent the oscillations amplitude but the signal detected at the photodiode which is proportional to that value. According to Fig. 1(a), we could obtain good resolution working in the range 0.5 to 0.1 eV. However, we observed that working at very low values implies that the tip is closer to the sample and therefore, the risk of crushing or sample modification (movement of the NPs because of the tip-sample interaction) increases. On the contrary, large values reduce the resolution of the images. Hence, in our experience, the best working condition are intermediate values as, in this case, 0.3 eV. Working with these parameters we obtained the image shown in Fig. 1(b) for a mica substrate. As the profile in Fig. 1(c) shows, the roughness is about ~0.4 nm, low enough to observe NPs with few nanometers size.

2.2.2 Sample preparation
In order to observe individual NPs, they must be dispersed in liquid solvents. For these NPs capped with polar molecules the solvent was ethanol white toluene or tetrahydrofuran was used for NPs capped with non polar species. Approximately 1 to 10 mg of the sample were dissolved in 50 ml of the appropriate solvent. The solution has to be colourless in order to achieve a good dispersion of the NPs, which is essential to obtain nanoparticles. These solutions containing the nanoparticles were sonicated for at least five minutes. Immediately after the sonication one or two drops of these solutions were deposited onto cleaved mica and they were allowed to evaporate under ambient conditions for one hour.

3. RESULTS
3.1 Observation of individual NPs
Figure 2 shows the Pd nanoparticles protected by tetrabutylammonium salts. Although TEM studies [3] revealed that the particle metallic cores were approximately spherical with average size about 2.4 nm, in the AFM images the particles width is fairly larger than their height. Actually, the average height obtained from the AFM measurements is similar to that obtained from HREM studies, whereas the average width is about 25 nm.

These results can be understood considering that AFM measures the interaction between the tip and the sample, and keep a constant distance between them. The tips have some thickness at the end, which is in the order of tens of nanometers. Thus, as it is explained in Fig. 3, the profile of the tip lateral displacement when scanning over a NP will be at least its width, that is clearly larger than the NP size. On the contrary, the maximum height of the tip matches quite well the size of the NPs. Therefore, when measuring small NPs with the AFM, all the information related to the particle size must be obtained from the height curves.

![AFM Profile of the tip displacement when scanning over the NP.](image)

In order to determine the best imaging conditions we measured amplitude vs distance, obtaining the curve shown in Fig. 1(a).
Formally, it should be possible to get information about the particle size from their width, considering that the image is the convolution of the NPs and the tip. However, the tip geometry is difficult to characterize and can be modified during operation because of occasional crash with the sample, so it is better to analyse the NPs height to obtain information about their size.

A more detailed comparison analysis of the information obtained by AFM and TEM can be performed comparing the size histograms obtained by both methods. Figures 4(a) and 4(b) show AFM images obtained from thiol capped Au NPs. Once again, we found that the width of the NPs is always larger than 20 nm, while the height is in the 1 to 5 nm range. The size histogram corresponding to the height presented in Fig. 4(d) results almost identical to that obtained by TEM [2]. This confirms the fact that measuring the height of the NPs we obtain appropriate results about the NPs diameter.

3.2 Observation of aggregates
As stated above, one of the advantages of AFM is that it allows the observation of some features as possible aggregate states of the particles on different substrates. In Fig. 5, we observe AFM images of silver NPs on silicon wafers, which are less dispersed (increasing their concentration on the substrate) or reducing sonication time. The NPs tend to form rings when they are deposited onto the mica substrate. In this case, it is possible to observe the individual NPs as well as the agglomerates. The agglomerate rings are about 1 micron size, and the particles are likely to join the ring, although some of them appear also inside the ring. In these images it is also possible to observe individual NPs distributed onto the substrate.

However, if the NP have a strong tendency to aggregate, it may not be possible to observe them individually. As an example, Fig. 6a shows thiol-capped silver NP. Optical measurements confirmed that NPs were spherical and smaller than 10 nm size. From the AFM images, the particle height (Fig. 6b and 6c) is between 2 and 2.6 nm with a maximum in 2.3 nm, whereas the width is above 100 nm (Fig. 6d). This width is too big to consider that they are individually isolated and, in this case it can not be due to the tip geometry. Taking into account these results, it seems that NPs are laterally aggregated. The aggregation is so strong that AFM resolution produced Au NPs, which were less dispersed (increasing their concentration on the solvent) or reducing sonication time. The NPs tend to form rings when they are deposited onto the mica substrate. In this case, it is possible to observe the individual NPs as well as the agglomerates. The agglomerate rings are about 1 micron size, and the particles are likely to join the ring, although some of them appear also inside the ring. In these images it is also possible to observe individual NPs distributed onto the substrate.

4. CONCLUSIONS
In summary, we showed that it is possible to observe small NPs (size 1-5 nm) with a standard AFM. To this purpose, the substrate and measurement conditions must be optimised, since we are close to the resolution limit of the technique. Information about NP geometry must be obtained from their height, while the width is largely distorted by the tip geometry. AFM imaging of NP results complementary to TEM measurements and allows studying the aggregation of NPs. However, the only analysis of the NPs using AFM, without other techniques may lead to large mistakes if the particles are aggregated.

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Another remarkable feature we observed was that the NPs seemed to grow with time. In average, for each day after the sample preparation, the particle height increased about 4 nm per day during the five days after deposition. This effect is probably due to the deposition on the NPs surface of some chemical species present in the air. Such effect will be dependent on the capping species and the environment, but it is worthy to bear it in mind in order to avoid mistakes in the measurement of particle size. Hence, it is important to perform the measurements just immediately after the sample preparation.

FIG. 4. (a) AFM image from Au thiol-capped NPs and (b) the 3D representation. (c) Height profile along the line indicated in (a). (d) Particle size histogram obtained from the height of the NPs.

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FIG. 5. AFM images from Au NPs protected by ammonium salts showing aggregation rings.

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FIG. 6. (a) AFM image from Ag thiol-capped NPs and (b) the height profile along the line in the figure. (c) and (d) represent the height and width histograms respectively (obtained from several images).

References:


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