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To see or not to see: Imaging surfactant coated nano-particles using HIM and SEM

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ABSTRACT

Nano-particles are of great interest in fundamental and applied research. However, their accurate visualization is often difficult and the interpretation of the obtained images can be complicated. We present a comparative scanning electron microscopy and helium ion microscopy study of cetyltrimethylammonium-bromide (CTAB) coated gold nano-rods. Using both methods we show how the gold core as well as the surrounding thin CTAB shell can selectively be visualized. This allows for a quantitative determination of the dimensions of the gold core or the CTAB shell. The obtained CTAB shell thickness of 1.0 nm–1.5 nm is in excellent agreement with earlier results using more demanding and reciprocal space techniques.

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1. Introduction

Today, nano-particles can be synthesized with a variety of shapes [1–5] and arrangements [6,7], allowing for different applications. To unveil the full potential of these nano-particle based applications [8,9] in general, it is imperative to understand and characterize the wide range of intriguing properties of these nanoscale entities. Important structural and compositional information can be obtained from high resolution imaging of these particles in their native form. It is crucial to realize that not only the shape but also the nearly always present surfactant layer influences the properties of the nano-particles [10].

Scanning Electron Microscopy (SEM) is routinely used to obtain information on the shape, size and arrangement of nano-particles. This method is very successful in this research field as it is minimal invasive and can achieve the required resolution of a few nanometers down into the sub-nanometer range [11]. With the advent of new detectors that allow energy filtering and separation of the different contributions to the signal as well as the possibility to use ultra-low acceleration voltages, the surface sensitivity of the method has also increased substantially. Alternatively, a new charged particle scanning beam microscopy method has entered the market a few years ago. Helium Ion Microscopy (HIM) [12] has an ultimate resolution as small as 0.29 nm [11,13] and a very high surface sensitivity [14]. It uses helium ions to generate a multitude of signals including secondary electrons (SE), backscattered helium (BSHe) and photons.

Despite their obvious advantages, both methods—SEM [15] as well as HIM [16]—are plagued by carbon deposition in the scanned area. This carbon deposition reduces image quality and in particular hinders the detection of ultra-thin carbon layers intentionally present on the sample. HIM is particularly sensitive to this effect for two reason. First, helium ions with a typical energy of 30 kV are very efficient in cracking hydrocarbons present on the sample surface. These hydrocarbons are either present on the sample and/or replenished from the vacuum during imaging. Second, due to the high surface sensitivity of HIM already very thin layers of carbon will be visible in the image. In particular the last point also applies for very low-voltage SEM. However, applying appropriate cleaning procedures to the chamber as well as the sample prior to imaging this problem can be eliminated. Provided that deposition of carbon from the chamber vacuum can be excluded a very high sensitivity for intentionally deposited ultra-thin carbon layers is possible in HIM [14].

As a result of the surfactant assisted fabrication routes nano-particles are usually covered by such a thin carbon based layer. In the case discussed here, gold nano-rods are covered with an interdigiting double layer of cetyltrimethylammonium (CTA) which is formed during synthesis using CTA-bromide (CTAB). Comparison of Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM) measurements revealed that the thickness of this shell is between 1.0 nm and 1.5 nm [17]—and thus less than the length of a single stretched CTA molecular ion of 2.2 nm [18].

In this paper we will present high-resolution images of CTAB/Au core-shell nano-particles obtained with SEM and HIM. In this

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context the underlying reasons for the visibility of either the gold-core or CTAB-shell in the different imaging modes will be discussed. By comparing core and shell we show that the thickness of the CTA layer can be measured with sufficient accuracy reducing the necessity for more elaborate measurement strategies such as SAXS and TEM.

2. Materials and methods

2.1. Nano-rod preparation

CTAB-stablized gold nano-rods of aspect ratios 4 and 5 were synthesized using a seed-mediated synthesis [5]. To remove excess CTAB from the suspensions, they were centrifuged at 15,000 rpm for 10 min. The supernatant was carefully removed, leaving the sedimented nano-rods in the bottom of the centrifuge tube. Finally, the nano-particles were resuspended in the same amount of Milli-Q water. This procedure was performed twice. In addition, the suspensions were centrifuged at 5600 rpm for 5 min to eliminate most spheres from the suspension. Ultraviolet-visible (UV-VIS) spectroscopy was used to identify typical resonances in the as-prepared nano-particles consisting of rods and some remaining spheres. The longitudinal peaks were situated at 800 nm and 860 nm for nano-rods of aspect ratios 4 and 5, respectively. The corresponding rod lengths amount to 45 nm $\pm$ 5 nm for aspect ratio 4 and 55 nm $\pm$ 5 nm for aspect ratio 5. The width of all rods is between 10 nm and 12 nm. Samples were prepared for HIM and SEM analysis, by drop-casting 30 μl of each suspension onto a clean SiO_2 substrate. Within 2 h the liquid has completely evaporated, leaving a coffee-stain ring of gold nano-particles. No further sample conditioning was necessary for the subsequent SEM and HIM imaging.

2.2. Charged particle beam microscopy

HIM measurements were performed using an ultra-high vacuum (UHV) Orion Plus helium ion microscope from Zeiss [16]. The microscope is equipped with an Everhardt–Thornley (ET) detector for Secondary Electron (SE) detection. A micro-channel plate situated below the last lens just above the sample allows the qualitative analysis of Backscattered Helium (BSHe). This detector yields images in which dark areas correspond to light elements—having a low backscatter probability—and bright areas—with a high backscatter yield—correspond to heavy elements in the specimen.

High Resolution Scanning Electron Microscopy (HRSEM) measurements were performed using a Merlin Field Emission SEM (FE–SEM) from Zeiss. The microscope is equipped with an on-axis in-lens secondary electron detector as well as a high efficiency off-axis secondary electron detector. The in-lens detector—which has been used in this study—is a high efficiency detector for SE1 and SE2 and owes its superb imaging results to the geometric position in the beam path and the combination with the electrostatic/electromagnetic lens. This detector is in particular powerful at low voltages provided a small working distance can be reached.

2.3. Simulation methods

In order to asses the yield and origin of secondary electrons as well as backscattered electrons in SEM, Monte Carlo simulations using CASINO [19] have been utilized. The sample was modeled using a 2 nm thick carbon layer on a 10 nm thick gold slab on top of a silicon substrate. The density of the carbon layer has been manually set to 0.5 g/cm^3. Secondary electron and backscattered electron yields were calculated as well as the Z_{max} distribution.

SRIM [20] calculations have been used to obtain insight into the contrast ratios for backscattered helium images. Backscatter yields for nano-rods and CTA covered silicon were calculated using the Kinchin–Pease approximation. The same sample setup as above has been used with the exception that the carbon layer has been replaced with a layer of CTA stoichiometry and a density of 0.5 g/cm^3.

3. Results

In Fig. 1(A) a HIM image of gold nano-rods is presented. The image has been obtained from an area covered by several layers of nano-rods. An acceleration voltage of 34.9 keV and an ion dose of 1×10^{17} cm^{-2} were used. Although the alignment of the rods is visible, the blanket covering them makes the recognition of individual rods difficult. This blanket is formed from residues—mostly CTAB—of the nano-rod synthesis. However, a SEM image of the same area is presented in Fig. 1(B). An acceleration voltage of 0.7 keV and a probe current of 50 pA has been used to record the image. Here, the rods are clearly visible and the CTAB blanket is only visible where it is very thick (e.g. in the upper right corner of the hole). The effect of the blanket is best seen by comparing the area marked with an arrow. From the two crevices visible in the SEM image one is not visible at all while the other is barely visible in the HIM image.

Fig. 2 shows high resolution HIM images and cross sections obtained from an area with a low density of gold nano-rods. The image has been recorded using an acceleration voltage of 20 kV and

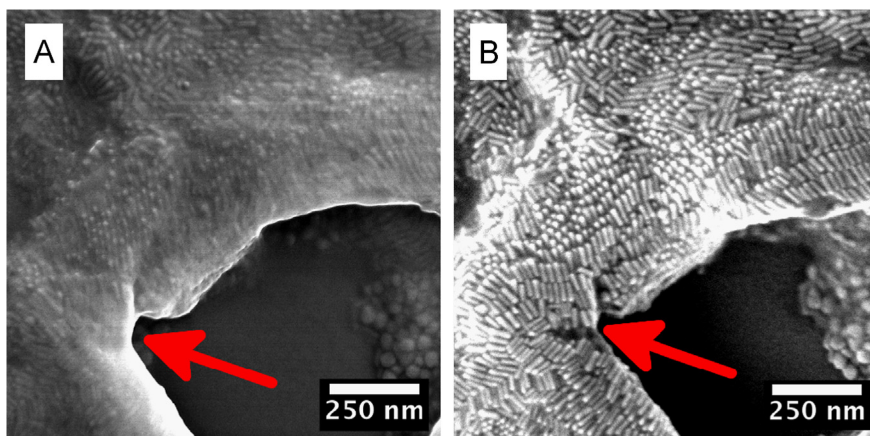

Fig. 1. Comparison of HIM and SEM images obtained from drop casted gold nano-rods. (A) HIM SE image recoded with 35 keV at a working distance of 6.5 mm. (B) SEM image recorded at 0.7 keV using the in lens detector and a working distance of 1.3 mm.

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