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# Conductivity mapping of nanoparticles by torsional resonance tunneling atomic force microscopy

C. Prastani,<sup>1,a)</sup> A. Vetushka,<sup>2</sup> A. Fejfar,<sup>2</sup> M. Nanu,<sup>3</sup> D. Nanu,<sup>3</sup> J. K. Rath,<sup>1,a),b)</sup> and R. E. I. Schropp<sup>1,a)</sup>

<sup>1</sup>*Utrecht University, Faculty of Science, Debye Institute for Nanomaterials Science, Nanophotonics—Physics of Devices, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands*

<sup>2</sup>*Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, 162 53 Praha 6, Czech Republic*

<sup>3</sup>*Thin Film Factory, Foeke Sjoerdwei 3, 8914 BH Leeuwarden, The Netherlands*

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In this paper, torsional resonance tunneling mode atomic force microscopy is used to study the conductivity of nanoparticles. SnS nanoparticles capped with trioctylphosphine oxide (TOPO) and with In<sub>2</sub>S<sub>3</sub> shell are analyzed. This contactless technique allows carrying out measurements on nanoparticles without destroying them and to obtain simultaneously topography and conductivity maps. This made it possible to achieve complete characterization of individual particles in a single measurement. The results demonstrate that the particles have conductive properties. The results have also showed that the TOPO capping layer may hinder tunneling currents, therefore should be avoided when performing these measurements. © 2012 American Institute of Physics.

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The necessity to improve local conductivity measurements led to the development of techniques for nanometer-scale electrical characterizations. For this type of measurements, usually, two different setups are used; conductive atomic force microscope (C-AFM)<sup>1–3</sup> and tunneling AFM (TUNA),<sup>4</sup> depending on the range of currents involved. The first is used to measure current in the range of sub-nA to  $\mu$ A, the latter for the range between sub-pA to nA.<sup>5</sup> However, both techniques are performed in contact mode; this makes it hard to investigate materials, which need low lateral or vertical forces because the standard forces of the AFM tip easily damage or deform the sample during the measurements. For this reason, contact mode is not applicable to study the topography and the conductivity for soft materials. Tapping mode can be a solution to study the surface morphology of soft samples without destroying them, because during these measurements the cantilever oscillates at its fundamental flexural resonance. Indeed, under these conditions, the lateral forces, which are the causes of the damage to the samples, are eliminated and the vertical forces are reduced. Furthermore, another advantage is that the AFM tip spends only short time in contact with the sample. But there is one main disadvantage; tapping mode is much less compatible with conductivity measurements, which need near-field interactions, such as TUNA.<sup>6</sup> Theoretically, it would be possible to use tapping mode for conductivity measurements, but this possibility is still beyond the current technology. During a tapping mode measurement, the tip is in contact with the sample for a few microseconds. To detect the current in such short time, it needs a current amplifier with a bandwidth in the range of MHz at a gain around 10<sup>9</sup>–10<sup>11</sup> V/A.<sup>7</sup>

It is known that the AFM cantilevers can oscillate in different modes, including torsional resonance (TR) mode. In 2003, Huang and Su<sup>8,9</sup> introduced an AFM mode to overcome the limitations described in the last paragraph. They used the TR amplitude (or phase) to control the feedback. The main advantage of this mode for TUNA is that low-force scanning can be performed while the tip is kept in the near-field, which allows obtaining tunneling currents. Moreover, compared to scanning tunnel microscope (STM), TR-TUNA AFM has important benefits. Since the feedback signal is not the tunnel current, as in case of STM, but the lateral forces, it is possible to study non-conductive samples. Moreover, this technique allows also to simultaneously obtain topography and current maps. Finally, the preparation of the samples for TR-TUNA AFM measurements is much faster than that for STM measurements. In Fig. 1, a schematic illustration of the working principle of TR-TUNA AFM is shown.

Two piezo plates (blue color in Fig. 1) are incorporated into the tip holder and are used for the excitation of torsional oscillations<sup>10</sup> only and do not interfere with the scanner piezo. They extend and retract in Z-direction. The interface between the AFM-tip and a sample during the AFM measurement is not well defined. It can be just the tip, air, and the sample for the ideal case, but at ambient conditions, it is most probable that at the interface there (because of the air humidity) are contaminants etc.

A lock-in amplifier is used to measure the amplitude and the phase of the cantilever. The feedback maintains a constant lateral tip/surface interaction by constant torsional amplitude and phase, the output signal adjusts the Z position. In the end, a DC voltage is applied between the tip and the sample. TR-TUNA AFM has been applied to study the surface of liquids<sup>11</sup> and the conductivity in carbon nanotubes.<sup>12</sup> Furthermore, since in a common tip, the height is 10–20 times shorter than the length, the torsional detection is 10 or even 20 times more sensitive than the flexural detection.

<sup>a)</sup>Present address: High Tech Campus 5, 5656 AE Eindhoven, The Netherlands.

<sup>b)</sup>Author to whom correspondence should be addressed. Electronic mail: J.K.Rath@uu.nl.

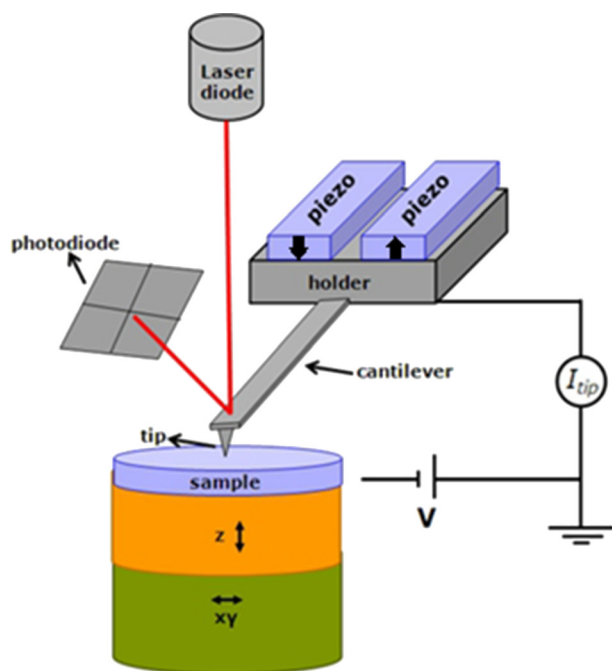


FIG. 1. Illustration of the working principle of TR TUNA mode.

Due to its special characteristics, TR-TUNA AFM can be an optimum method for the electrical characterization of nanoparticles. For applying nanoparticles in devices such as solar cells<sup>13</sup> or transistors,<sup>14</sup> it is not enough knowing the optical properties; it is indispensable to study their electrical properties. In this work, TR-TUNA AFM has been applied, to study nanoparticles. The samples were measured by Veeco Dimension 3100 AFM equipped with an extended TUNA module for the current detection in the pA range. It has conductive coating of Cr/Pt on both sides. For TR-TUNA mode, we used BudgetSensors ElectriMulti75-G cantilevers with the force constant about 3 N/m, resonant frequency about 75 kHz, and the torsional resonance frequency about 400 kHz.

It is shown in this paper that by means of this technique, it is possible to study the size and shape of the nanoparticles and simultaneously obtain a map of the electrical current. For these experiments, SnS nanoparticles were chosen because of their interesting physical characteristics, such as high optical absorption and proper band gap for photovoltaic

applications.<sup>15</sup> SnS nanoparticles capped with trioctylphosphine oxide (TOPO) were used for this experiment. They were synthesized by a colloidal route and deposited on an etched heavily doped n-type silicon wafer, by drop casting on the substrate. It is important that the substrate is as smooth as possible because it is impossible to detect them if the roughness is not negligible compared to the dimensions of the nanoparticles. A bias of  $-1$  V was applied between the sample and the tip and it was kept constant during the measurements. The voltage is negative to prevent local anodic oxidation.<sup>16,17</sup> Moreover, during the measurements, there is always an interface layer on top of the sample, sometimes it can be even a layer of water from humid air. A negative voltage allows the tip to get through this layer and making it sure to measure the sample and not just surface adsorbates. In Fig. 2, two images, analyzed by wSXM software,<sup>18</sup> corresponding to the topography (a) and the current (b) of SnS nanoparticles detected by TR-TUNA AFM are shown. Despite that the measurements are noisy, in the topography image, it is still possible to identify nanoparticles though it is hard to distinguish single particles. It is possible to recognize a region of the sample with a high density of particles (Fig. 2(a) black circle). Comparing the topography image with the map of current, it is possible to see an analogy, mostly corresponding to the section with a higher density of nanoparticles, because their contribution to the current is higher and thus easier to detect. The current measured is rather low and also this image is noisy. Even with higher voltage of  $-10$  V, the image did not improve. As mentioned, TR-mode is a non-contact mode, therefore, it is unlikely that the tip coating was somehow damaged. However, the problem of the tip contamination is probable and can be one of the reasons of the visible noise in AFM images.

The high noise level can also be due to the presence of TOPO. Indeed, TOPO does not allow the tip to approach the particles properly, disturbing the measurement and making the images unclear.

To overcome this issue and for verifying our assumption, keeping the nanoparticles in solution, the TOPO from the SnS nanoparticles was removed by acid treatment, using HCl, and the particles were capped by an  $\text{In}_2\text{S}_3$  shell by means of chemical bath deposition.

Afterwards, the same TR-TUNA AFM measurements were carried out. This time a bias of  $-10$  V has been applied

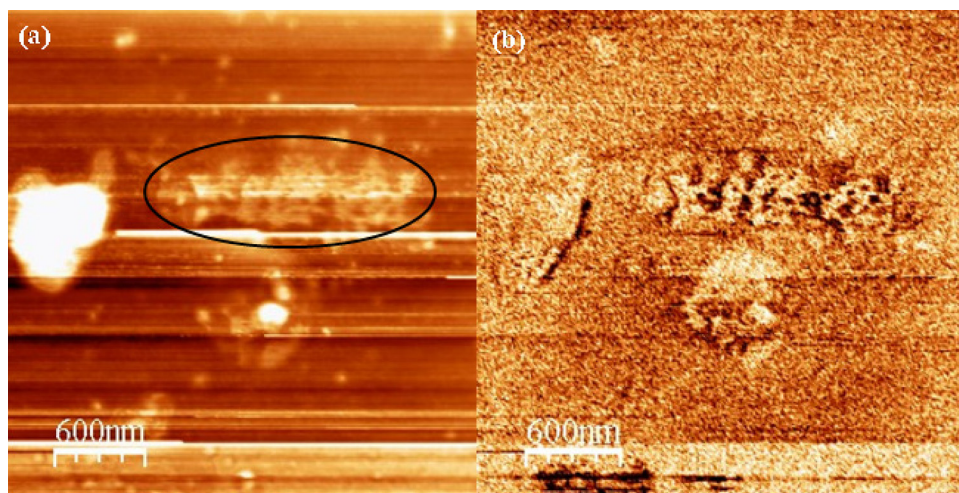


FIG. 2. Topography (a) and current map (b) of SnS nanoparticles acquired by TR-TUNA AFM.



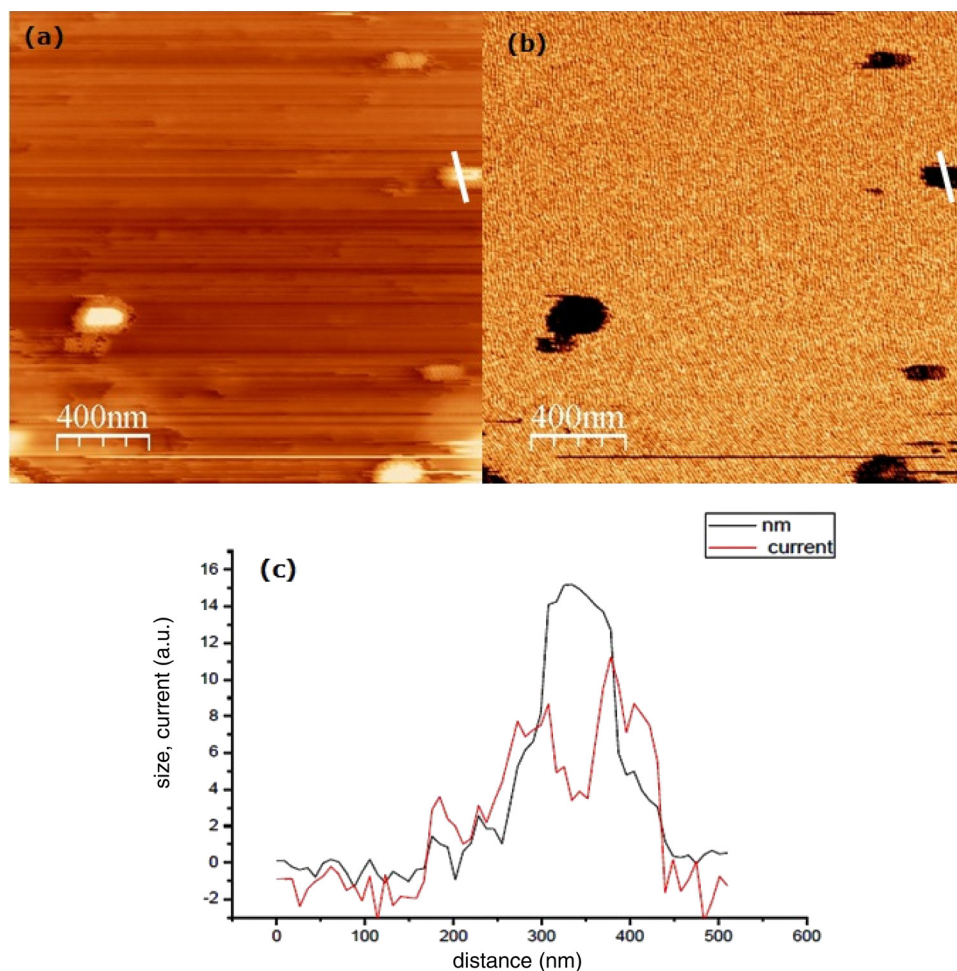


FIG. 3. Topography (a) and current map (b) of SnS/In<sub>2</sub>S<sub>3</sub> core-shell nanoparticles acquired by TR-TUNA AFM; (c) profile of the size and the current on a single nanoparticle.

between the sample and the tip. Figures 3(a) and 3(b) show the topography image and the map of current, respectively, of the SnS/In<sub>2</sub>S<sub>3</sub> core-shell nanoparticles. Now it is possible to distinguish the particles and moreover, the correspondence between the topography image and the map of current is evident. Quantitative information has been obtained studying the profile of one nanoparticle, marked with a white line as shown in Figs. 3(a) and 3(b). Furthermore, Fig. 3(c) shows a plot of the size of the nanoparticle (black curve) and the current of the nanoparticle (red curve) along the white marked line. The size of the feature is 15 nm. The two curves have the same profile except for the center; the black curve shows indeed a peak that fits perfectly with the shape of the nanoparticle while the red curve shows a dip. This can be explained considering the tip: when the tip is on the side of the particle, the surface of the tip near the particle is larger, hence, the detected tunnel current is also higher than when the tip is on top of the particles, where the surface is only a few nanometers and the current is lower. The evidence of the current proves that these nanoparticles are conductive and hence, they can be used in electronic devices. From a quantitative analysis, the maximum current value in Fig. 3 is 400 fA and the Z-scale in Fig. 2(b) is 200 fA.

In this work, the capability of TR-TUNA AFM to study the electrical behavior of nanoparticles has been demonstrated. The main advantage of this technique, compared with other AFM-based techniques, is the possibility to study simultaneously morphology and conductivity of soft materi-

als. This gives the opportunity to obtain a complete characterization on a single nanoparticle. Moreover, it has been also found that when performing this type of measurements, the TOPO type cappings should be avoided because it prevents the tip from controllably approaching the particle.

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