

Reply to “Comments on Electric-Field-Assisted Growth of Highly Uniform and Oriented Gold Nanotriangles on Conducting Glass Substrates”

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We appreciate the comments of Diao et al. on our recently published paper,^[1] which describes the characterization of gold nanotriangles (NTs) using optical absorption spectroscopy, atomic force microscopy (AFM), and X-ray diffraction (XRD). AFM images of the NTs, which confirmed their morphology, were provided, but scanning electron microscopy (SEM) images were not. Here SEM, AFM, and optical images are presented, which suggest that NTs are indeed formed. Each comment has been addressed below.

It is well known that artifacts—caused particularly by blunt tips—can appear in AFM measurements. However, after considering the following facts, we are convinced that NTs were genuinely observed. In order to confirm the formation of the NTs, samples were imaged using dynamic force microscopy (DFM, a non-contact AFM technique) at the facilities of another research group (Seiko SPA-400); the results were confirmed for both the parent and the NT surfaces.^[1] Various control measurements were performed.

Figure 1a–c show AFM images recorded at various stages of growth. NTs of varying size as well as spherical particles can be seen. The particle size increases with the evolution of reaction time. Note that a blunt tip could not have produced images of spherical particles and uniform NTs with sizes that varied systematically as a function of reaction time. Non-contact-mode imaging (using an AFM-CRM 200 microscope, WiTec GmbH) of the NTs was also conducted using a fresh cantilever. Since the tip interacted with the sample for only a short time, degradation of the tip or sample was unlikely. The non-contact-mode topographic and phase AFM images of NTs that were synthesized under optimized conditions are shown in Figure 1d,e. Most of the NTs observed had an edge length of 400–450 nm. There were small variations in the NT dimensions, even with synthesis under optimized conditions. Some areas, which appear as channels void of NTs in between two layers of NTs, are also observed (Fig. 1f). Such an image would not be likely if artifacts were indeed responsible for the results obtained. Other morphologies, such as spheres, are also observed. In addition, it is clear that a large number of lower-lying NTs are stacked and appear to be fused. This is further confirmed by the SEM images. If the tip was worn

out or contaminated, the image would have shown separate NTs. However, in this case, the NTs are not well separated, but stacked on top of each other; some of the NTs even lie in different planes.

The SEM images taken from different areas of the indium tin oxide (ITO) using a FEI QUANTA-200 SEM microscope show the presence of stacked NTs of the same dimensions observed in the AFM images (Fig. 2a,b). Because of the large edge-length/thickness ratio, the NTs often appear fused and stacked. Corresponding energy dispersive analysis of X-rays (EDAX) data support the formation of Au NTs. The NTs were deformed by the electron beam, as is evident in Figure 2c. In the SEM images, underlying spherical nanoparticles can be clearly seen. The presence of such nanoparticles on different areas of the substrate may explain the increased ratio of the intensities of the (200) and the (111) peaks in the XRD spectra, since diffraction data were taken from very large areas compared to the areas used for the AFM scans.

It was possible to increase the edge lengths of the NTs by slow reduction of Au ions on the surfaces of the growing NTs.^[2] The sizes of the NTs synthesized according to the reported procedure^[1] could be increased by treatment with excess Au³⁺ and ascorbic acid, allowing imaging of large NTs via optical microscopy (Fig. 2d; WiTec GmbH, CRM 200). Even though several equilateral NTs are observable in such images, their orientations are different from those of the parent NTs.

In the UV-vis absorption spectra, the feature at 520 nm can be attributed to the transverse plasmon absorption, as is the case for other anisotropic structures. In addition, possible spherical particles below the surface may contribute to this feature. Only well-structured gold NTs can produce a UV-vis-near-IR absorption spectrum, as indicated in our original paper. Therefore, being able to obtain such a spectrum with characteristic features of gold NTs is in itself a clear indication that NTs are formed. For large numbers of truncated triangles, hexagons, and microplates, the spectra are different.^[3] The red-shift in the near-IR absorption spectra with respect to the spectra presented by Shankar et al.^[4] may be due to the coupling of the surface plasmon resonances of the triangles, which is caused by the uniform stacking of the individual NTs and their close proximities (as can be seen in the microscopy images). Synthesis of uniform NTs requires optimization and even small changes affect the results significantly.^[1]

A 0.1 mM cetyl trimethylammonium bromide (CTAB) solution of NTs appears turbid at 0 °C. However, upon warming to room temperature by keeping the solution for some time under ambient laboratory conditions, a clear solution was obtained. The sample was cleaned by washing repeatedly with water to remove

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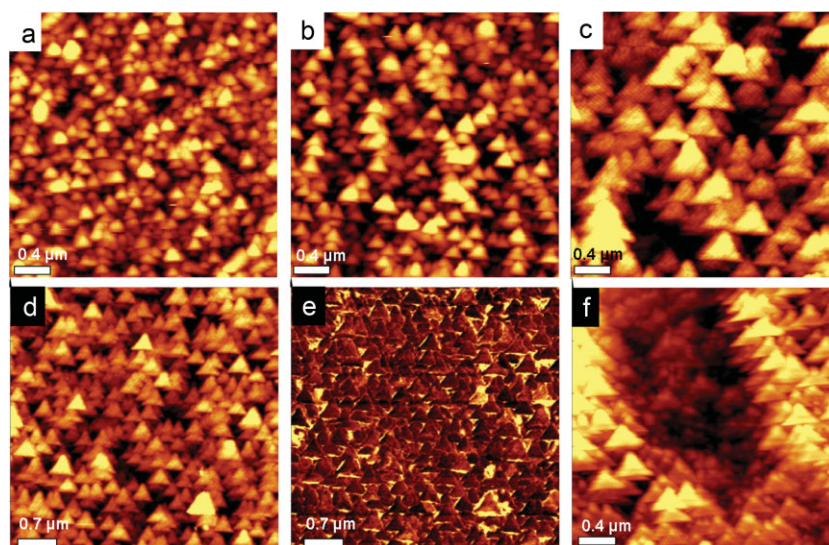


Figure 1. Contact-mode AFM images ($3 \mu\text{m} \times 3 \mu\text{m}$) of the NTs formed after different time intervals: a) 20 min, b) 30 min, and c) 1 h. Image (b) was presented in the original paper [1]. Images (d,e) are topographic and phase images ($5 \mu\text{m} \times 5 \mu\text{m}$), respectively, of the NTs analyzed in the non-contact mode. f) Contact-mode AFM image ($3 \mu\text{m} \times 3 \mu\text{m}$) of the indium tin oxide (ITO) substrate after NT growth, where the center appears as a channel void of NTs that sits between two NT layers. It is clear that other morphologies, such as spheres, are also present in certain areas.

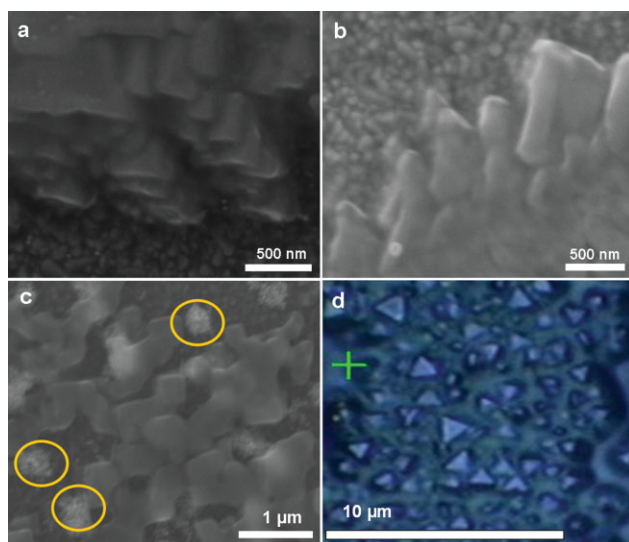


Figure 2. a,b) SEM images of the NTs formed on the ITO surface; stacking of the NTs is clearly seen. c) SEM image showing NTs deformed by impact of the electron beam. Underlying spherical NPs are marked with circles. d) An optical image of larger uniform NTs grown on ITO.

CTAB and other reagents. The washing process did not remove the NTs since they were firmly attached to the ITO.

In view of the facts presented, we are convinced that the results indicate the electric-field-assisted formation of NTs and were not caused by artifacts of AFM.

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