AFM Induced Self-assembling and Self-healing Mechanism of Silicon Oxide Nanoparticle Linear Array Domains Templated on Moiré Superlattice Patterns on HOPG

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Abstract

Silicon oxide nanocluster suspensions were drop-cast on highly oriented pyrolytic graphite (HOPG) and investigated using ultra-high vacuum non-contact atomic force microscopy (AFM). The assembly of silicon oxide nanoparticle arrays was observed during consecutive scanning of the surface using AFM. The patterns and alignments of the nanoparticle arrays were consistent with templating on a Moiré pattern in the top layers of the HOPG substrate. By halting and restarting the scanning process it was shown that the formation of nanoparticle arrays was driven by the AFM scan itself. Vacancy defects identified within the nanoparticle arrays were found to fill over time with nanoparticles; it was demonstrated that diffusion was preferred along the symmetry lines. This ‘self-healing’ mechanism was also shown to be driven by the AFM scanning. The recovery of defects within the arrays, and other observations of array dynamics, implied that the nanoparticle arrays had liquid-like qualities.

Key Words: Self-Assembly, Self-Repair, Silicon Oxide Nanoparticles, AFM, Moiré Superposition Patterns
1 Introduction

The physical and chemical properties of nanoparticles often alter with size, and can differ dramatically from the properties of the same materials in bulk [1–3]. These unique properties of nanoparticles might enable their use in various applications, for example in catalysis [4], nanoelectronics [5], biodiagnostics [6], sensors [7], bioimaging [8,9], biolabeling [10], and many more. While a considerable variety of nanoparticles have been reported and studied in the literature [11–13], silicon-based nanoparticles have received particular consideration because of the importance of silicon as a semiconductor material in electronics, but also because of their fluorescence properties, which are in stark contrast to their non-fluorescent bulk counterparts [8,14].

The ability of nanoparticles to self-assemble at interfaces and surfaces in both two and three dimensions is another driver for further applications. Nanostructures generated from self-assembled nanoparticles have the potential for application in nano-engineering and nano-architecture [15–17]. Previously, it was reported that self-assembling structures might find application in a range of areas such as nano-antennae [18,19], biomolecule detectors [20,21], sensors [22,23], nano-optoelectronics [24], and nanoscale conductors / semiconductors / insulators [25]; it is therefore important to understand the mechanisms underlying nanoparticle self-assembly. Furthermore, it has also been shown that the physical properties of nanoparticles can alter when organised into superlattices [26]. Therefore, understanding and control of the surface structure and assembly process is essential to achieve nano-engineering applications [15]. Templating, as we have investigated in this paper, appears to be one of more simple and cost-efficient methods for control in self-assembly [23,27].

HOPG is often used as a substrate material for nanoparticle deposition. It provides a number of advantages such as easy cleaving using Sellotape and can provide an atomically flat, clean,
weakly interacting surface with very few defects [28]. The structure of HOPG resembles multi-layered graphene [29]. Therefore, the physics of nanostructure self-assembly on HOPG can be directly related to self-assembly on graphene [30,31]. The AFM-induced self-assembly mechanism reported in our paper is templated by superlattices, which were formed due to interference patterns called Moiré patterns. Moiré patterns have been previously reported on HOPG due to slight shifts or the rotation of the uppermost layer of the graphene in the HOPG with respect to the underlying layers [32,33]. The Moiré pattern repeats the honeycomb structural motif of the underlying graphene. Rabe et al. reported that the Moiré patterns on HOPG are able to direct and order molecules such as alcohols and lipids into ‘stripe-shaped’ structures [34]. In our previous work [31] we reported that silicon oxide nanoparticles had been drop-cast onto freshly cleaved HOPG, forming nano-stripe arrays. Two types of structures, one following the zigzag and the other following the armchair directions of symmetry, were identified. This demonstrated that the linear structures followed the HOPG Moiré superlattices, providing further evidence that the formation of linear structures – as templated by Moiré patterns – is a favoured mode of growth during the dewetting of a drop-cast colloidal solution.

In this work, and to the best of our knowledge for the first time in the literature, the direct visualization of the formation of 2D silicon oxide nanoparticle linear array domains, as templated by Moiré patterns, has been reported. In addition, the self-healing ability of the defects on these domains on HOPG was evidenced and investigated using non-contact AFM at room temperature.

2 Material and Methods

2.1 Nanoparticle Synthesis
The nanoparticle solution used in the experiment was prepared in a special Ultra-High Vacuum (UHV) production system. A magnetic sputter head was used as the source to generate silicon atoms in the system. The silicon atoms so generated collide with each other and, through gas aggregation, form nanoclusters in the production chamber. The nanoparticle beam was directed into the deposition chamber and then deposited on a liquid nitrogen-cooled target while water vapour was sprayed onto the same target to produce a nanoparticle-water ice matrix. The frozen ice matrix thus formed was then heated and collected as a nanoparticle suspension. A detailed description of the production process can be found in our previous papers [35,36]. The technique enabled us to produce a clear, stable, silicon oxide nanoparticle colloid solution.

Optical absorption and fluorescence spectra initially suggested a structure of a silicon oxide shell with a silicon-rich core. Further analysis of the data, using a quantum confinement model, showed that the core was less than 1.5 nm in diameter. This size information agreed with an analysis of the colloidal stability using a simple particle-particle interaction model [37] and also with an AFM study of single and double layers of nanoparticles produced by drop-casting of colloidal suspension on HOPG, showing that the end-over-end diameter was between 2 and 3 nm [38].

Subsequent analysis of the nanoparticles using FTIR spectroscopy confirmed the presence of SiO$_2$ in the colloidal suspension [39]. XPS analysis of the nanoparticles deposited on HOPG and various other substrates showed strongly shifted 2$s$ and 2$p$ silicon peaks, suggesting that the fraction of unoxidized silicon was close to zero [39,40].

The silicon oxide nanoparticles produced in this way exhibited a number of extraordinary properties: upon photoexcitation in the UV spectral range they emitted an intense fluorescence band centred around 420 nm. Trials extending over more than a year showed that this
fluorescence was maintained, indicating remarkable structural stability within the colloidal suspension.

2.2 Thin Film Preparation

Nanoparticles were deposited on HOPG (Highly Oriented Pyrolytic Graphite) using the drop-cast method. A HOPG crystal was cleaved with Sellotape, resulting in a fresh, clean surface for deposition. The silicon oxide nanoparticle solution was prepared in pure water using our special production method [35], and then diluted with isopropanol (IPA). It was found that laboratory wash-quality isopropanol (IPA) or ultra-pure HPLC grade IPA (Sigma-Aldrich) did not have any significant effect in the chemical and physical structures; accordingly, we chose to use laboratory wash-quality IPA in our experiments. The nanoparticle suspension was diluted in various ratios (1:15, 1:20, or 1:30 depending on the desired concentration) with IPA using a micropipette in a vial. 5 µl diluted solution was taken from the mixture and drop cast on a HOPG crystal (Pi-Kem, 0.8⁰ mosaic spread) under a laminar flow hood. The amount of mixture in this dilution factor was sufficient to produce a single layer nanoparticle thin film on the HOPG crystal. When the drop contacted the surface, it instantly spread over the surface and dried within seconds. The HOPG crystal was then transferred into a fast-load chamber of an Omicron Nanotechnology AFM and left in vacuum overnight. The vacuum chamber of the AFM was allowed to achieve a 10⁻⁹ mbar base pressure, after which the sample was transferred to another chamber where the AFM measurements were performed at 7.2 10⁻¹⁰ mbar.

2.3 Microscopy Work

An Omicron Nanotechnology UHV atomic force microscope (AFM) was used for our measurements, which were performed in non-contact, constant force mode at room temperature. A SiN tip (Micromasch) with a cantilever resonance frequency of 307 kHz was used in the AFM measurement. The radius of the tip was about 20 nm and had a nominal
cantilever stiffness of 40 nm$^{-1}$. The HOPG step edges were used to calibrate the AFM, where a constant step height of 3.4-3.6 Å was anticipated [43]. Hundreds of consecutive scans were made in this investigation, with the entire set of measurement taking several days to complete. The scanning direction was chosen so as to be perpendicular to the cantilever’s long axis. One complete scan that the system can perform consists of four images in four different scanning directions. Two scans were obtained from bottom to top and top to bottom, each of which gave two images, scanning from left to right and right to left. Consecutive scans were recorded by the system. One complete scan took about 45 minutes depending on scanning speed. The images used in our evaluations use the same scanning direction to avoid possible tip convolution effects. The raw AFM data was correlated and processed using WSXM [41] and the change in size of the defect islands and nanoparticle linear array islands were evaluated using the ImageJ software (ImageJ bundled with 64-bit Java 1.8.0_112) [42].

3 Results and Discussion

3.1 Silicon Oxide Nanoparticle Arrays Templated on Moiré Patterns After Dewetting

A drop-cast of the solution of isopropanol-diluted silicon oxide nanoparticle suspension with various dilution factors (1:15, 1:20, 1:25, 1:30 depending on desired concentration) was applied to the HOPG crystal, and the sample was investigated by AFM to examine the formation of silicon oxide nanoparticle arrays.
Figure 1: (a) AFM image of linear nanostructures observed for a dilution factor of 1:20 after dewetting during the drop-cast process. At such low concentrations, no complete linear nanoparticles arrays were observed whereas many partly formed linear array domains could be observed. The blue line in the image indicates where the height profile was recorded. (b) The height profile of the blue line in Figure 1 (a).

We distinguish here between two different formation mechanisms for nanoparticle arrays: (a) formation of nanoparticle arrays by dewetting of a drop-cast nanoparticle suspension on the surface (see Figure 1 and 2), and (b) tip-induced formation of nanoparticle arrays (described in section (3.2)).

In our previous work, we reported that the nanoparticle arrays followed a Moiré pattern [31]. It was seen that two types of orientation model could be identified, which were the zigzag and armchair types (see Figure 2). When zigzag and armchair domains appear next to each other on an identical HOPG domain they can be easily identified by the characteristic separation between the stripes. This is illustrated in Figure 2 (d), which has been reproduced from [31], where the AFM image shows the region where the zigzag- and armchair-oriented nanoparticle arrays meet. The arrays belonging to the zigzag orientation were aligned towards the on the left side of the image with a separation of 5.5 nm; the arrays belong to the armchair orientation,
which was oriented towards the right side of the image with a separation of 6 nm in this instance. It was also reported that the orientation type determines the stability of the nanoparticle arrays, where the zigzag orientation was found to be more stable than the armchair orientation since the nanoparticle arrays would have more active vertices per unit area than in the zigzag orientation.

The AFM image and cross-sections in Figure 2 nicely show the higher degree of the structure of the nanoparticle arrays that follow the zigzag direction. The armchair array appears laterally more blurred and defect-free. Also, the cross-sectional height-profile is less-structured, corroborating the liquid-like nature of the arrays that follow the armchair directions.

Figure 2: An illustration of fully developed linear arrays. (a) The AFM image for a dilution factor of 1:15 is presented in the image. The blue line shows where the height profile was taken. (b) The mean of eight neighbouring height profiles obtained around line b in image (a) is shown. (c) Mean of eight height profiles obtained around line c in the image (a). (d) AFM image showing nanoparticle arrays formed in the zigzag and armchair directions. Blue lines show where the height profiles were taken. (e) Height profile of arrays formed in the zigzag direction. (f) Height profile of nanoparticle array formed in the armchair direction.
3.2 Self-Assembling Silicon Oxide Nanoparticle Arrays Templated on Moiré Patterns

To study the tip-induced formation of nanoparticle linear array domain formation, a 1:30 isopropanol-diluted silicon oxide nanoparticle suspension was drop-cast onto the HOPG crystal and the sample thus formed was investigated by AFM. More than 380 consecutive AFM scans were performed in non-contact and constant height mode at a random region of the HOPG crystal. The first AFM scan results showed that the silicon oxide nanoparticles were randomly dispersed on the HOPG substrate and achieved only sparse coverage of the surface (see Figure 3 and Figure 4 showing the surface of the region investigated). No visible or clear array formation was seen in the first images where the early formation process started at the thirty-fourth scan. Some nanoparticles had accumulated on the edges of the HOPG steps, whilst others had produced discrete agglomerated regions. The average height of the nanoparticles on the surface was in the range 1.3-1.6 nm. An HOPG layer almost at the centre of the region investigated can be identified. The step height of the layer was measured as being 0.36 nm, which is in agreement with similar values reported in the literature [43].

During the measurement, the scanning region was not changed but small drifts due to thermal changes or mechanical shifts occurred. The shift was corrected manually, but in almost all scans clean regions on the HOPG, especially in the mid-section and on the left side of the images, could be easily identified. While some nanoparticles changed position, others formed aggregates which changed in size during the scans. It was found that some nanoparticle-aggregates were ultimately diminished in size, and that they decomposed on the surface.

The most important observations obtained from our investigations were those pertaining to the self-assembling arrays (please see supplementary video). The nanoparticle arrays are shown in Figure 3 with arrows, where the arrays consisted of nanometre-sized stripes aligned parallel to
each other and displayed identical structural characteristics to the nanostructures described in our previous paper [31]. The width of the single stripe varied between 6 and 8 nm.

Figure 3: a) AFM image illustrating the tip-induced formation of linear arrays after a long period of repeated scanning. The image pertains to scan number 196 of a series of 380 scans (see text). The IPA dilution factor was 1:30. The arrows in the image show a variety of nanoparticle arrays that had self-assembled on the HOPG crystal.
Figure 4 shows a selection of the 380 images that were chosen to illustrate the size change of the nanoparticle arrays. The numbers on the left or right corner at the top of the images shows the AFM scan number. The arrays are circled in the images; different colours have been used to identify the different arrays. The first visible and apparent array formation was observed in scan 34, and was tagged with a black circle (see Figure 4). In scan 34, the array consisted of two arrays aligned parallel to each other. After a couple of scans, these two arrays came together and ultimately merged, remaining in this state as the size of the domain started to increase. Various other arrays started to form immediately after the formation of the first, which are indicated with arrows in Figure 3 and 4 (see supplementary video for details). It was observed that the size of the arrays changed during the scan, which was thought to occur due to the AFM tip scan itself. To test the validity of this hypothesis, the AFM scan was paused during scan 48 for 10 hours, after which the scan was continued; however, no visible change in the size of the array was observed. The change in size of the first array (indicated by a black circle in Figure 4 and a black arrow in Figure 3) was investigated, the results of which are presented in Figure 5.
Figure 4: Examples of AFM images obtained. Numbers in the top corners of the images indicate the scan number of a series of images obtained in consecutive order. Circles were used to show the arrays. Different colours were used to identify the various self-assembled arrays.

As stated above, a drop-cast 1:30 isopropanol-diluted silicon oxide nanoparticle aqueous suspension was investigated, where the 1:30 dilution factor was of such a low density that no visible or clear linear array formations were seen in the early images. This was also seen in the graph presented in Figure 5, where size data about array formation is presented. The size of the array increased whilst the surface was being scanned. The red line in the graph shows the period
during which the scans were paused. It can be seen that no significant change in the size of array occurred during this time. In addition, after the pause, the size of the array remained essentially the same for the subsequent 10 scans, after which it began to rapidly increase. The stability of the array size during this period was attributed to the array being in a dynamic equilibrium. When the dynamic equilibrium was broken, the size starts to increase again. The size of the array reached its maximum around scan number 120. Between scans 120 and 170, the array size fluctuated slightly but otherwise remained essentially unchanged. After scan 170, the size of the array began to decrease drastically before its ultimate decomposition at scan 306.

Regarding the graph, such size change behaviour of the nanoparticle arrays enabled us to determine that the AFM surface scan had a direct effect on array formation. While pausing the scan, the size of array 1 increased, though no activation or change of the position of other particles on the surface could be detected. Other arrays on the surface showed essentially identical characteristics. It can be seen in figure 4 that the domains tagged with green and yellow circles also showed similar characteristics to array 1. They first tended to increase in size, stay essentially stable, and finally diminish in size and decompose. The size analysis of other arrays could not be performed due to their position. They formed at the edge of scanning area and some parts of the arrays formed and remained out of the AFM scanning region where no accurate size measurement could be conducted.

The size measurement graph of array 1 showed Gaussian-like characteristics (see Figure 5). It was suspected that drop-casting the nanoparticle suspension on the surface left some small nanoparticle (possibly even single nanoparticle) residues on the surface. It was proposed that they were extremely small and could move sufficiently quickly on the surface that the AFM tip would be unable to detect them (when moving on the surface). We hypothesise that scanning the surface with the AFM tip transferred energy to the surface; after reaching a certain energy
barrier, the energy applied by tip activates the nanoparticles. Two possible scenarios were proposed for the activation of nanoparticle array formation: that the nanoparticles became trapped by a defect, or there was nucleation followed by agglomeration of nanoparticles in stripes due to collisions, forming two-dimensional arrays. The striped shape of the arrays was templated by the superposition of the hexagonal structure of HOPG layers in the Moiré templating we observed in previous work (see our previous papers for details, e.g., [31]). Whilst the AFM tip was scanning the surface, nanoparticles that were otherwise freely moving on the surface could become caught by defects on the surface or agglomerate, eventually forming nanoparticle arrays.

Visual inspection revealed that the nanoparticle arrays had a liquid-like structure with highly active periphery. Free nanoparticles attach or detach from the active periphery of the array, resulting in an attendant increase or a decrease in array size, respectively. In the instance where the number of attaching nanoparticles ($N_a$) is greater than number detaching ($N_d$) ($N_a > N_d$), then clearly the array size will increase, and vice versa. As scanning the surface activates the free nanoparticles on the surface, a long-period scan will cause nanoparticles to leave the scanning region as there is no barrier to such translations. With regards to the Gaussian characteristics of the size increase graph and size-change behaviour of the arrays, it can be understood that the formation of nanoparticle arrays occurs randomly as a result of the stochastic behaviour of nanoparticles under the influence of the AFM cantilever. It was also thought the arrays formed by tip induction were directed in armchair orientation. Since the nanoparticle linear array arrays have fewer active vertices per area, the nanoparticles are less stable and gradually decompose after formation.
3.3 Self-Healing Defects on Silicon Oxide Nanoparticle Linear Array Domains

In the previous section, tip-induced assembly of silicon oxide nanoparticle arrays were discussed. As discussed in section 3.1, arrays could also be formed during the dewetting of the silicon oxide nanoparticle suspension when drop-cast on the HOPG substrate, provided a critical minimum concentration was reached. We occasionally encountered self-assembly of nanoparticle arrays, an example of which was reported in section 3.2, as discussed.

Figure 5: An illustration of increasing and decreasing array size induced by the scanning process. The red hatched stripe shows the time where the scan was stopped for 10 hours. The green arrow shows the moment (scan 36) where the first self-assembled array was observed. Double-tip effects were taken into account in the size determination.
For the case reported in this section, the nanoparticle suspension was diluted with isopropanol in a 1:15 ratio, a concentration high enough to cause self-assembly of arrays, drop cast on the HOPG crystal and investigated using AFM. More than 220 scans were performed on a random region of the HOPG crystal, the first results of which showed large nanoparticle arrays aligned on the surface, as expected. Seeing the arrays in the first image, and indeed the images obtained from subsequent scans, corroborates the fact that these arrays formed during or after dewetting of the nanoparticle suspension and that tip-effects were negligible in terms of array formation.

Figure 6 shows four characteristic images of this series of scans. Small defect arrays on both the HOPG crystal surface itself and the nanoparticle arrays were identified. In addition, nanoparticles were found to have randomly spread over the empty regions of the HOPG surface; these free nanoparticles were found to be 1.3-1.7 nm in height on average.
Figure 6: Four AFM images of the HOPG surface with a 1:15 dilution factor. Green and blue circles show self-healing defects in arrays. Yellow and blue arrows show dynamic changes on the surface. Numbers in the top-left corner show scan number.

The scanning region was maintained for the entire set of measurements, but the dimensions of the scanning region were increased twice during the scanning process. Small deviations were observed in the scanning region, which for the most part were due to thermal instabilities and mechanical shifts. The shifts occurred during the scans were subsequently manually corrected. The majority of the scanning region was found to be covered with
nanoparticle arrays, though some regions were found to be array-free, where a number of individual nanoparticles were found to have spread to surface after dewetting. A few nanoparticles were also observed in arrays, as indicated by the blue and green circles (see figure 6). A number of dynamical changes occurred whilst scanning. Most of the nanoparticles spread on the HOPG were stationary, but a very few (as indicated by the blue arrow in Figure 6) were observed to move during the scanning process. The stationary clusters were used as ‘landmarks’ for lateral calibration between consecutive images.
Figure 7: Series of consecutive images showing the self-healing mechanism of defect pit domain 1 (bright spot indicated with a blue arrow shows active repairing).

The most intriguing observation in this part of the investigation was the self-healing mechanism observed in the defect pit arrays within arrays. More than 220 scans were examined in order to track the self-healing of defects and appropriate illustrative scan images identified. Defect pit arrays were tagged with coloured circles in the scans shown in Figure 6. The self-healing of the defect observed in Figure 7 was tagged with green circles in Figure 6; those seen in Figure 8 were tagged with blue circles in Figure 6. The numbers at the top-left corner of each scan image give the appropriate ordering. It should be noted that the defect array tagged with a green line, as shown in Figure 6, was identified in the first scans, whilst the second defect array was identified after scan 10. Due to the shifts that occurred during scanning, the second defect was only identified later.
Figure 8: A series of consecutive AFM images showing the self-healing mechanism of defect array 2 (bright spot indicated with a blue arrow shows active repairing).

The AFM image for scan 1 in figure 7 shows an uncovered defect zone approximately 80 nm x 40 nm in area, which is five stripes in width. The stripes in both defect zone 1 and defect zone 2 were aligned in the same direction, and showed similar size-change behaviour. They tended to shrink quickly in the earlier scans, after which the rate of shrinkage appeared to slow down. In the investigation of both defect 1 and defect 2, a number of active regions in the
defects were identified, and are indicated with arrows in Figure 7 and 8. The change in size of defects 1 and 2 are shown in Figure 9. It was seen that the smaller defect healed faster than larger. The size and rate of healing appeared to be inversely correlated. We previously predicted that the nanoparticle arrays had a liquid-like structure and were very active; our observations of the self-healing mechanisms observed were fully in accord with our previous observations in this regard. Free nanoparticles are continuously wandering on the surface, and regularly attach and detach from the sides of arrays. However, the liquid-like arrays catch the free nanoparticles and ‘pump’ them towards the defect island. The bright regions in the domains were considered to be active sites where the repairing mechanism was ongoing, and it seems very likely that this is an indication of free-moving particles being transferred to the defect by aligned nanostripes. Whilst the nanoparticle supply was directed away from active sites to the defect zones, no vacancies or defects appeared to form in the arrays, which also supports the hypothesis that the linear domains have a liquid-like structure. The active sites in the defects are agglomerations of nanoparticles pumped into the defect, where those nanoparticles act as a ‘repair agent’. The nanoparticles wander inside the defect and attach to the defect walls. The nanoparticles attaching to the defect wall form new stripes. The formation process (self-repair process of the defects) was followed by the use of AFM on a frame-by-frame basis.
Figure 9: Observed change in size of defects. The green dashed line shows the scan number at which the second defect area was identified.

5 Conclusions

In this paper, AFM-induced self-assembly and self-healing mechanisms of silicon oxide nanoparticle arrays, as templated on a Moiré pattern on HOPG, were studied. Two distinct formation processes were found for nanoparticle arrays – after dewetting of a nanoparticle suspension when drop-cast onto HOPG, and self-assembling formation – were exemplified.

The first result section briefly introduced the formation of arrays as templated on a Moiré pattern. Zigzag- and armchair-type formations of arrays were observed in our measurements, and the effects of the dilution of the nanoparticle solution on the formation process were demonstrated. For this type of concentration-controlled formation process, arrays existed from the very first image onwards.
The second section considered the tip-induced assembly of nanoparticle arrays. Clear evidence for this type of assembly mechanism was that a randomly chosen area in which arrays were initially absent resulted in the progressive formation of nanoparticle arrays while consecutive scans were performed. When scanning was stopped for more than 10 hours, the size of the arrays did not change. After restarting the scan, the arrays were again found to grow. It was also found that under the influence of the tip, nanoparticles were activated and able to leave the scanning region. This process counteracted the growth of the arrays, eventually leading to shrinking and dissolution.

In the third result section, the self-healing mechanism of nanoparticle arrays was investigated. Two defect pits were identified in the scan region, within which active spots were observed. It was seen that the active zones play a vital role in the healing process. It was proposed that nanoparticle arrays were in a liquid-like state, and that they ‘pump’ nanoparticles into the defect zone, where pumped nanoparticles actively move and ‘fix’ the defect. Their active motion left bright regions in the scan where the tip could detect any form of stable structure. It was proposed that scanning the AFM tip over the surface activated the nanoparticles, giving them the energy to translate from one place to another. In addition, in both the investigations into self-assembling and self-healing nanoparticle arrays, a number of large nanoparticles were detected that were found to change their positions with scan number. This was observed in many of our experiments and will be reported on in detail in future publications. The change in position of these large nanoparticles during the AFM scans was also an indication of the influence of the AFM tip upon the nanoparticles.

The understanding of the formation of large arrays both without and under the influence of an AFM tip is of great importance for the engineering of nanoscale structures at surfaces. The fact that novel silicon oxide nanoparticles exhibit the formation of such domains may aid in the development of optical devices, sensors and nanoantennae, for example by deposition of metal
films onto the linear domains. Our findings may also be important for the interpretation of related observations [44].

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7 References


