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# Effect of annealing temperatures on the self-assembly properties of iron (III) oxide nanoparticles

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**ABSTRACT**

*The use of Atomic Force Microscopy (AFM) to investigate the effect of different annealing temperatures on the self-assembly properties of Iron (III) oxide nanoparticles prepared by the Langmuir-Schaefer method is experimentally demonstrated and discussed. Ferritin molecules containing a self-assembled core of iron oxide undergo thermal treatment to produce the nanoparticles. When the Iron (III) oxide nanoparticles were subjected to annealing temperatures, they were found to coalesce especially at the boundary of the graphitic substrate to conserve energy. At higher temperatures the particles were again seen to coalesce more, forming islands at the graphitic boundary. Further studies revealed that these islands represented different phases of Iron (III) oxide nanoparticles that resembled$\gamma$-$Fe_2O_3$, $\alpha$-$Fe_2O_3$and a third phase that likely was a combination of $\gamma$-$Fe_2O_3$ and $\alpha$-$Fe_2O_3$.*

**Key words**: Nanoparticles, Atomic Force Microscopy, Annealing,

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## INTRODUCTION

According to Cientifica [1], Nanotechnology is a major technology for the future compelling many Governments in the world to commit billions of hard-earned dollars in its development.A nanoparticle (or nanopowder or nanocluster or nanocrystal) is a microscopic particle with atleast one dimension less than 100 nm. Nanoparticle investigation is currently an area ofpassionate scientific research due to a wide variety of potential applications in biomedical,optical and electronic fields. Nanoparticles are of immense scientific interest as they areeffectively bridge between bulk materials and atomic or molecular structures [2].The popularity of nanoparticles has soared recently owing to their peculiar size as well as optical, electronic, magnetic, and chemical properties that depend on the crystal size [3]. As a result of their physical and chemical properties, nanoparticles have the potential to benefit the electronic device development, Medicine, Catalysis and the use of remedial methods to improve skills or reverse environmental damage [4, 5, 3]. Nanotechnologies are already being used in the food packaging industry [6]. Moreover, Nanotechnology is significant in the electronic properties of materials which vary much with high reduction in particle size especially when quantum mechanical effects are considered. These properties are mostly observed within nanometre range [7]. Furthermore, the Computer and data storage branch is gaining support from nanotechnology to improve performance.Non-volatile memory device, a technique based on the application of silver nanoparticles has been manufactured [8].

One such nanoparticle that shows a lot of promise because of its unique traits for the advancement of many indispensible fields of endeavours is Iron (III) oxide. For instance, due to their magnetic properties, super

paramagnetic behaviour and toxic influence on brain cancer cells; they are used simultaneously in medicine as tools for tumour imaging, treatment of brain cancer, and other Cancer therapy [9, 10]. These particles have also proven to be more effective than conventional-sized particles (in microns) for oxidizing CO decomposition of biomass by annealing [11]. Aside their oxidizing potential, Iron (III) oxide nanoparticles can be used as adsorbent to remove metal from aqueous solutions [12, 13, 14].

An innovative approach to create nano-sized Iron (III) oxide particles is based on the capability of Ferritin to self-assemble and form a core of iron oxide. Ferritin is a significant iron- storage protein in living cells made up of a spherical hollow shell consisting of 24 polypeptide subunits capable of storing iron as hydrated iron oxide in the inner cavity [9]. Annealing the sample therefore removes the Ferritin shell to expose the nanoparticles. The morphology of this process and the behaviour of the formed Iron (III) oxide nanoparticles annealed at elevated temperatures are not well – established.

Therefore, this work seeks to investigate the morphology and effect of annealing temperatures on the self-assembly properties of Iron (III) oxide nanoparticles using Atomic Force Microscopy. Again, this work also seeks to provide answers and observations of Iron (III) oxide nanoparticles in the form of images as samples were annealed at different temperatures.

## MATERIALS AND METHODS

Highly Ordered Pyrolytic Graphite (HOPG) obtained from the Experimental Physics II Laboratory, University of Augsburg, Augsburg,were used as substrate for this experiment because of its organized layer structure, stability compared to others and particularly due to theweak Van der Waals forces bounding these layers; thus making their removal easy. The surface of this substrate was cleaned with isopropanol before Sellotapeswere used to cleave the surface of sample so as to avoid any possible dirt.About 80 ml solution was made from 0.01 M NaCl by adding 80 ml ultra-pure water to a weighed 46 mg NaCl powder in a clean beaker. These Beakers and other apparatus such as pipettes and test-tubes were pre-cleaned by soaking them in detergents overnight and then washed thoroughly in the morning with double deionized water to remove any possible contaminants. The solution was then whirled slowly to ensure that the salt dissolve completely in the solution. About 145 µl horse spleen Ferritin solution (0.15 M) was further added to the NaCl solution.

Preparation of the nanoparticles monolayers was achieved by using a complete Langmuir Blodgett experimental set – up based on Langmuir Schaefer technique as shown in Fig. 1. Detail information about the parts of set –up and their functions are presented elsewhere [16]. Contrary toLangmuir Blodgett method, the substrate is dipped horizontal into the solution when using the Langmuir Schaefer technique. These two methods enable one to produce and classify single molecule thick films with control over packing density of molecules. They also provide the chance to form multilayer structures with different layer composition. However, the Langmuir Schaefer method alone was used to prepare the nanoparticle monolayers for this workbecause it is a simple but accurate methodwith short turn-around – time. More importantly, it is relatively less costly compare to Langmuir Blodgett technique. Critical parts such as the trough are also pre – cleaned with chloroform to avoid possible contamination and hydrophobic.

The solution was then transferred onto the set – up trough for analysis. As a way of increasing the bond formation between the surface molecules and to make the surface conditions favourable for producing monolayers, about 14 µ$l$Octadecyltrimethylammoniumbromide (Tenside) was added to the solution.

Principal parameters such as pressure values, isotherm and details of surface tension of the solution were observed on the computer with the aid of a barrier mechanism during the experiment. The barrier mechanism and the isotherm are monitored on a computer untilan appropriate target pressure was reached before the cleaned face of substrate was quickly dipped horizontally on the surface of the solution in the trough. This pressure (about 20-26$dyn/cm$)was achieved after compression of the barrier and waiting for a few minutes. These samples later underwent annealing at temperatures in the range of 573K-733K and times 0.5 – 24 hours. The water and the Ferritin shells were then removed leaving the nanoparticles to be imaged for analysis.

In other to obtained precise images of the various nanoparticles in the Ferritin monolayers substrates in air, the Atomic force microscopy operated in the Tapping mode was used. In the tapping mode, the tip of the AFM touches

the surface and detaches from the sample surface for each oscillation cycle by using large vibration amplitude. The various images were then analysed using suitable computer software program.

**Fig.1: A complete Langmuir Blodgett set-up**

## RESULTS AND DISCUSSION

The following analysis is carried out on fifteen samples and the average results are as follows:

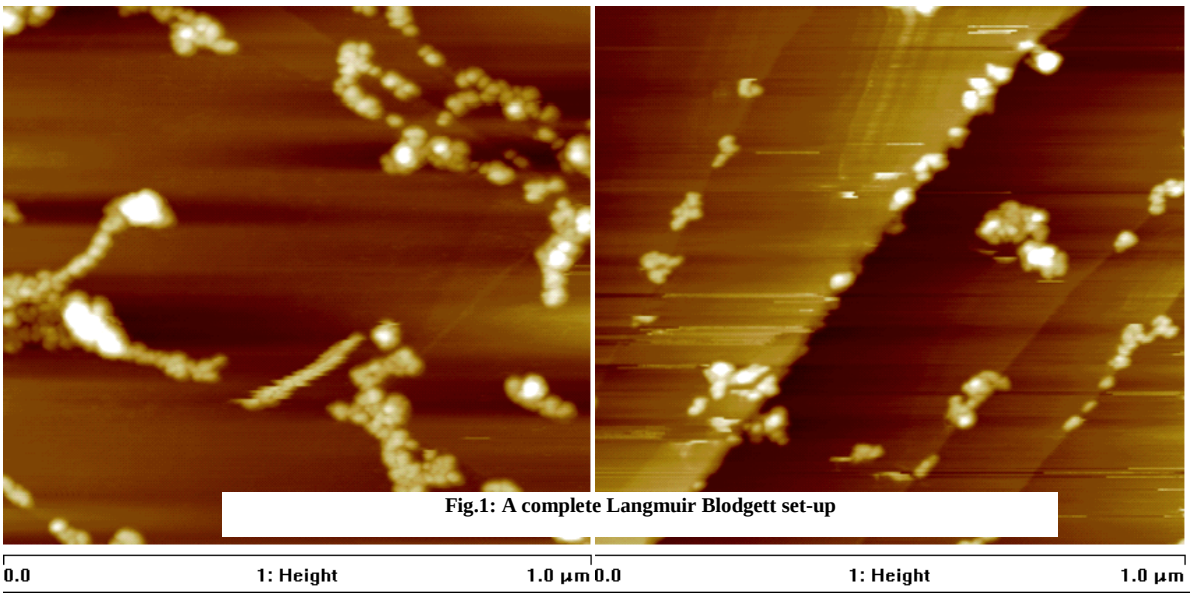


**Fig. 2 AFM image of an oxidized ferritin monolayer annealed for 1 hour**

**Fig. 3 AFM image of oxidized ferritin monolayer annealed at at 573K 573K for 25 hours**

Figs 2 and 3 give detailed revelations of the nanoparticles. Fig.2 shows samples heated for only 1hour at 573k illustrating clustering nanoparticles to reduce the surface energy. Fig.3 depicts sample heated for 573k at 25 hoursshow more cluster in addition to alignment of the nanoparticles at the graphitic boundary. Nanoparticles shownin Fig.3 are smaller than that in Fig. 2 because more water was lost when more heating was applied. It was observed that the surface energy of samples shownin Fig. 3 wasfurther reduced by alignment at steps of the substrate.

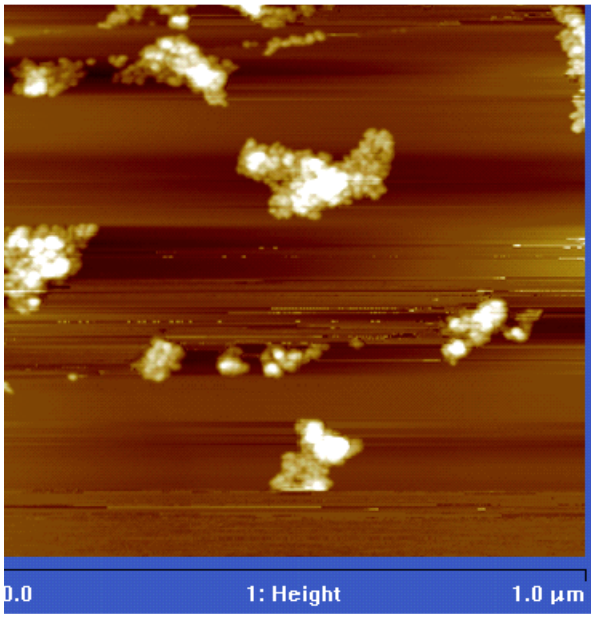


**Fig. 4 AFM image of an oxidized ferritin monolayer annealed at 673K for 0.5 hrs.**

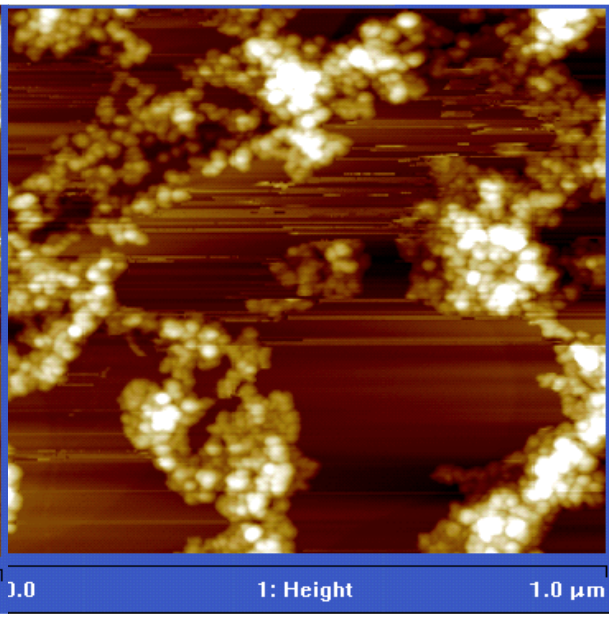


**Fig .5 Image of oxidized ferritin monolayer annealed at 673K for 2 hours**

Figs 4 and 5 present two different images as the temperature and the annealing time were increasedto 673 K. Therewere more nanoparticles in Fig.4 than Fig. 5. The nanoparticles in Fig.4 were sparsely distributed (like islands of nanoparticles) which could be due to the tip dragging some of the particles since some scratches could be seen on the image background. Sample images presented in Fig.5 also experienced the tip dragging of the nanoparticles but the extent were different for both images. The nanoparticles also appeared more compact and bigger thereby conserving surface energy than inFig.4. The grain boundaries for both images in (Figs 4 and 5) werenot visible.

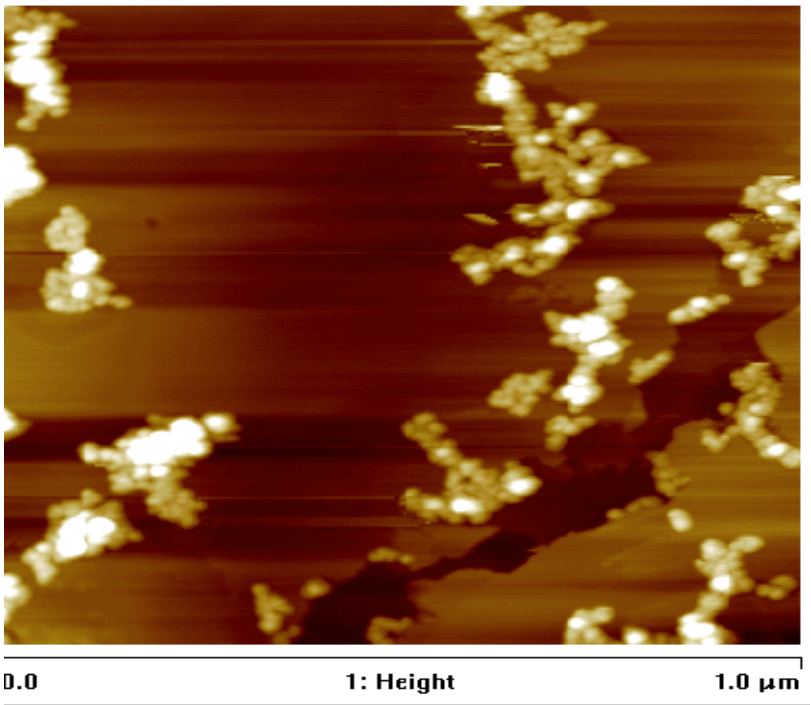


**Fig. 6 AFM image of an oxidized ferritin annealed at 733K for 25 hours**

Fig. 6 shows Nanoparticles annealed at 460°C (733K) for 25 hours respectively. The energy supplied was highest. Fig.6 shows more clustering of what, may be nanoparticles and theyappeared to be merged. Alignment at the graphitic grain boundary was also reduced to the minimum. One plausible explanation for this observed phenomenon is that, the substrate energy was lowest for nanoparticles shown in Fig. 6. Densely packed clusters of distinguishable nanoparticles were also revealed in the annealed sample images captured. Annealing the samples causes the removal of protein shell resulting in a lower coverage of the HOPG surface.

Thus,nanoparticle clusters consist of well-defined particles size of approximately 6.5-7nm. These sizes were expectedly reduced with annealing because of water loss. Dimensional analysis of the graphite boundary with respect to size, diameter, height and steps can be achieved with a computer software program, nanoscale.Thenanoscale program could also show a three dimensional image of each sample. Fig.7 showsthe use of the program for image measurements.

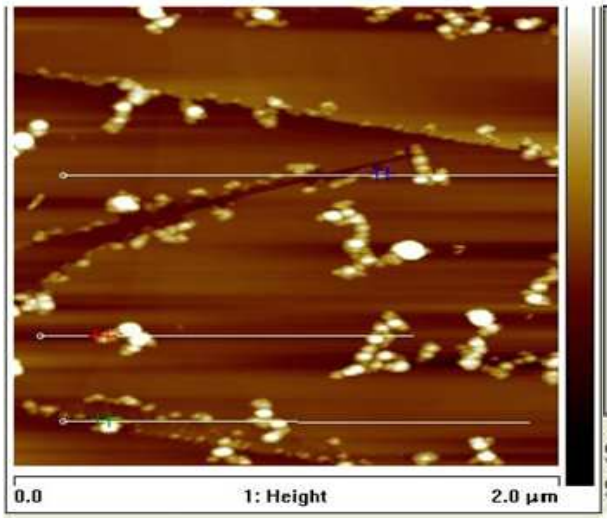


**Figure 7 AFM image showing size of nanoparticles**

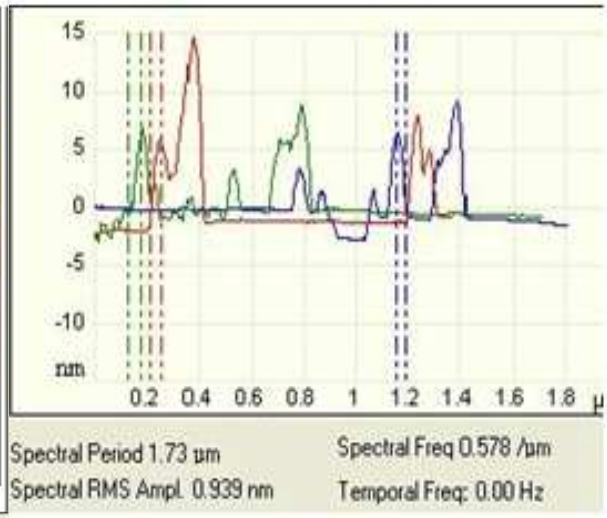


**Fig. 8 AFM Graphs showing the size of Iron (III) Oxidenanopaticles**

**Table 1 showing the various distances of the Iron (III) Oxide nanoparticles**

| Line Pair | Horizontal Distance(µm) | Vertical Distance(nm) | Surface Distance(µm) |
|---|---|---|---|
| Blue | 0.035 | -6.30 | 0.036 |
| Red | 0.043 | 7.057 | 0.044 |
| Green | 0.047 | 6.918 | 0.048 |

By taking a scan line at a sample surface one can readily obtain the corresponding information of the nanoparticles at the area.Fig.7 shows three different areas indicated by red, blue and green colours where information of the nanoparticles present and their heights indicated in Fig. 8 have been displayed in Table 1 above. Clusters werefound predominantly at steps present on the HOPG substrate surface. Clusters of the nanoparticles forms increasedwith a rise in annealing process. Formations of clusters also reduced the surface energy of the substrate.

## CONCLUSION

Thermal treatment of $Fe_2O3$nanoparticles shows that, an increase in annealing temperatures and times lead to clustering of the nanoparticles. The nanoparticles form self-assembled structures that lead to a reduction in surface energy of the system. Most of the nanoparticles were also found to cluster at the boundary of the graphitic substrate. We therefore conclude that, the graphitic boundary provides a favourable environment for cluster formation. Hence nanoparticles cluster at the boundary due to the minimum energy required to form there.

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