# Critical size of iron nanoparticles on liquid substrates*

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We study the iron atomic aggregates deposited on silicone oil surfaces by using atomic force microscopy. The aggregates are composed of disk-shaped nanoparticles with the mean diameter $\Phi_c \approx 31.7$ nm and height $H_c \approx 4.5$ nm, which are nearly independent of the nominal film thickness. The experiment shows that a material condensation process must occur in the nanoparticles during the growth period. The anomalous phenomenon is explained.

**Keywords:** critical size, nanoparticle, condensation behavior, liquid substrate

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## 1. Introduction

Due to the unique properties and potential applications in biomedical, optical, electronic, and other interdisciplinary fields, various nanostructures, such as nanotubes, nanoribbons, nanoparticles, etc., have been successfully fabricated and widely investigated.[1–5] In particular, their promising applications in catalysts, biosensors, and biomacromolecule delivery have been proved to be a fruitful success.[6–8] Meanwhile, as the nucleation and the growth of the nanostructures are sensitive to the substrates, the preparations based on different substrates have been studied and a great many fascinating results have been reported.[9–13]

Since the geometric size, morphology, and microstructure of the nanoparticles play an important role in the physical properties and practicalities,[14–16] much effort has been contributed to the control of the formation of the nanoparticles. In order to study the dynamic process of the nanoparticle formation, several *in situ* observation techniques have been introduced to control the size and growth of the nanoparticles.[17,18] Moreover, using ionic liquids to control and stabilize the nanoparticles is proved to be another promising method.[19–21]

In this paper, we successfully fabricate iron (Fe) atomic aggregates on a silicone oil surface and the morphology evolution from branched aggregates to a continuous Fe thin film is observed. The high resolution images measured by atomic force microscope (AFM) reveal that the aggregates consist of numerous disk-shaped nanoparticles. The average branch width of the aggregates and the mean diameter as well as height of the nanoparticles are independent of the nominal film thickness. We find that a material condensation process actually exists during the growth period of the nanoparticles.

## 2. Experiment

The samples were prepared at room temperature by thermal evaporation method and the experimental setup is schematically depicted in Fig. 1. The silicone oil (dow corning 705 diffusion pump fluid) was painted onto a frosted glass surface, which was fixed 135 mm below the tungsten filament. The pure 99.5% Fe was evaporated onto the silicone oil surface after the pressure of the vacuum chamber reached $2.0\times10^{-4}$ Pa. The deposition flux $f$ was fixed as 0.01 nm/s. The nominal film thickness $h$ varies from 0.03 nm to 2.00 nm, which was determined by a quartz-crystal balance (ULVAC CRTM) and calibrated by using an atomic force microscope (AFM, Veeco DI 3000). The dependence between the nominal film thickness $h$ and the deposition time $t$ reads $h = ft$. For most of the samples, since the maximum deposition time is less than 30 s, therefore the temperature of the samples during deposition may be considered as a constant, i.e., room temperature.[9]

After deposition, the sample was kept in the vacuum condition for six minutes and then removed from the vacuum chamber immediately. The Fe aggregates were separated from the oil surface to a piece of crystalline silicon wafer and then washed carefully with acetone and ethanol.[22] After that, an immediate AFM measurement in tapping mode was taken to observe the microstructure of the sample.

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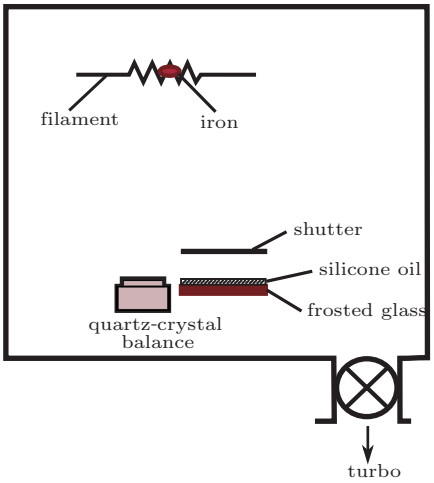



**Fig. 1.** (color online) Schematic setup of the experiment.

## 3. Results and discussion

Figure 2 shows the typical AFM images of the branched Fe aggregates on the silicone oil surfaces. One sees that the morphologies of the aggregates are different while the average branch widths of all the aggregates are similar, indicating that the formation mechanism of the aggregates can be traced to the two-stage growth model[9] and the study below refers to the second stage of the model. On the other hand, with the increase in the nominal film thickness $h$, the branched aggregates diffuse and grow on the silicone oil surface. If two aggregates meet, they may connect with each other. Therefore, as $h$ increases, the mean area of each aggregate increases obviously, as shown in Figs. 2(a) and 2(b). It should be noted that the average branch width of the aggregates in Fig. 2(a) is similar to that of the aggregates in Fig. 2(b).

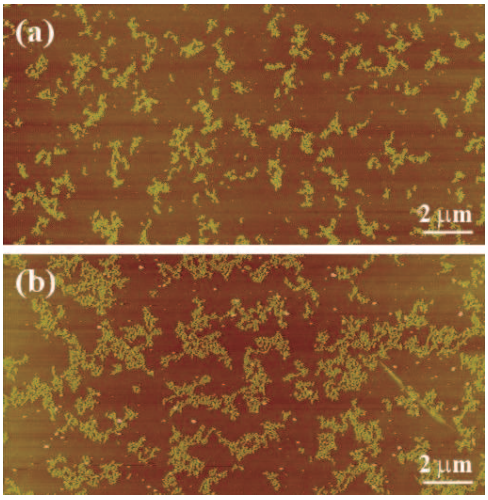



**Fig. 2.** (color online) Typical AFM images of the branched Fe aggregates deposited on silicone oil surfaces. The nominal film thickness: (a) $h = 0.03$ nm, (b) $h = 0.10$ nm. Each image has a size of 20.0 μm×10.0 μm.

In our experiment, a computer programme was used to calculate the apparent Fe coverage of the total area of the AFM image, namely $\rho$. The result shows that, for the samples shown in Figs. 2(a) and 2(b), the coverage $\rho = (11.08 \pm 0.44)\%$ and (18.90±0.97)%, respectively. According to this nonlinear dependence of $\rho$ on $h$, two possibilities may be suggested: (i) a material condensation process may exist and (ii) the height of the aggregates may increase during the growth period.

In order to further study the microstructure of the aggregates, high resolution AFM images are taken, as shown in Fig. 3(a). It is shown that the aggregates are composed of numerous nanoparticles, which is similar to the experimental observations in other metallic systems on liquid substrates.[23–26] It should be emphasized that all the nanoparticles in the aggregates stick together while the overlap among them rarely occurs, reflecting the weak attractive interaction among the nanoparticles. This result is similar to the previous finding in the Al system[23] and, however, totally different from those in the Ag and Cu systems.[25,26]

We measure the diameter $\Phi$ for all the nanoparticles in the aggregates and the result is displayed in Fig. 3(b). The Gaussian fit to the experimental data shows that the mean diameter of the nanoparticles $\Phi_c = 33.6 \pm 5.1$ nm, which is almost twice as large as the mean diameter of the nanoparticles in the Al system.[23]

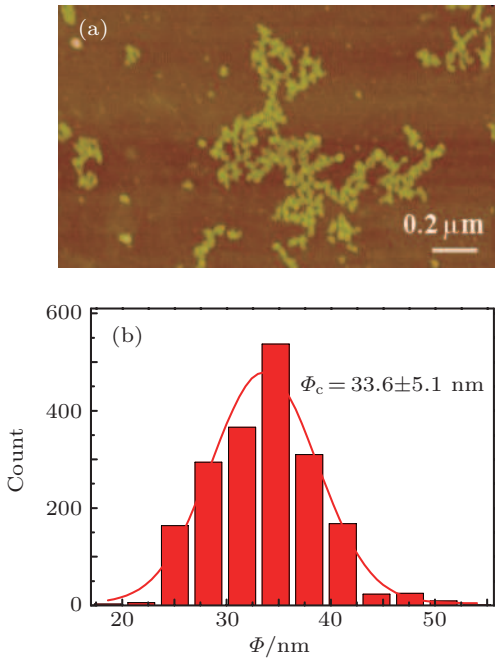



**Fig. 3.** (color online) (a) High resolution AFM image of the branched Fe aggregates. The nominal film thickness $h = 0.03$ nm and the image has a size of 2.0 μm×1.2 μm. (b) The diameter distribution of the nanoparticles in the aggregates for the sample shown in panel (a). The solid line is the Gaussian fit to the experimental data.

In order to further study the material condensation phenomenon in the nanoparticles, a series of experiments with different thickness $h$ was made and the diameter distribution of the nanoparticles for each experiment was measured. Figure 4 shows the dependence between the mean diameter of the nanoparticles and the nominal film thickness. It can be seen

that, as $h$ changes from 0.03 nm to 2.00 nm, the mean diameter $\Phi_c$ is almost independent of $h$, which reveals that a characteristic material condensation process may happen during the growth period. The inset AFM images show the morphology evolution of the samples from branched aggregates to a continuous thin film.

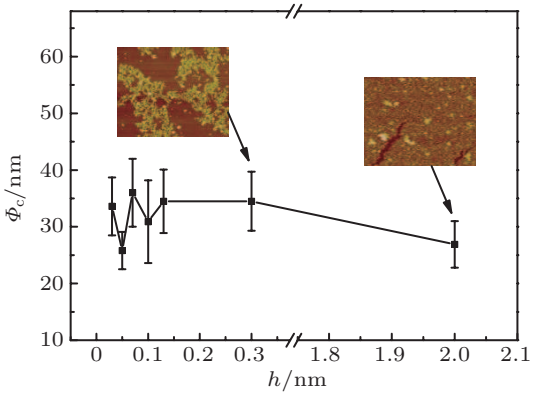



**Fig. 4.** (color online) Dependence of the mean diameter $\Phi_c$ on the nominal film thickness $h$. The insets show the AFM images of the branched Fe aggregates ($h = 0.3$ nm) and continuous Fe film ($h = 2.00$ nm). Each image has a size of 2.5 μm×2.0 μm.

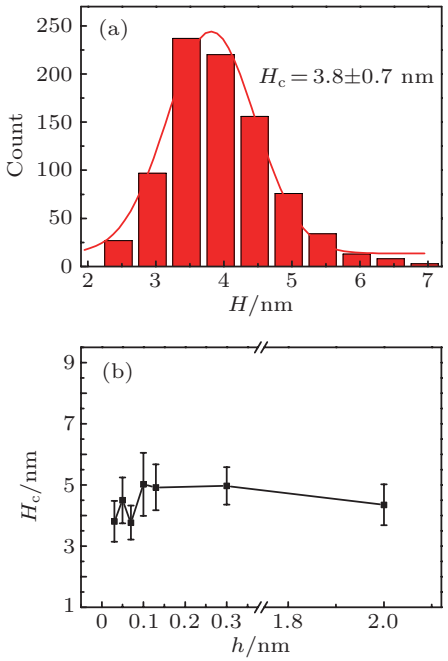



**Fig. 5.** (color online) (a) The height distribution of the nanoparticles in the aggregates for the sample with $h = 0.03$ nm. (b) The mean height of the nanoparticles versus nominal film thickness.

Meanwhile, an AFM measurement for the height of the nanoparticles, namely $H$, was carefully taken. Figure 5(a) shows the height distribution of the nanoparticles for the sample with $h = 0.03$ nm. The Gaussian fit reveals that the mean height $H_c = 3.8 \pm 0.7$ nm. We then measured the height distributions for the samples with different thickness $h$ and the dependence of $H_c$ on $h$ is displayed in Fig. 5(b), which shows again that $H_c$ is almost independent of $h$.

It is quite unexpected that, as shown in Figs. 4 and 5(b), both the mean diameter $\Phi_c$ and height $H_c$ are almost independent of $h$ as it changes from $h = 0.03$ nm to $h = 2.00$ nm. Mathematically, the average values of $\Phi_c$ and $H_c$ for all the samples are revealed to be 31.7 nm and 4.5 nm, respectively. If the overlap among the nanoparticles can be neglected, based on the values of $\rho$ and $h$, we may obtain the average number of the Fe atoms in each nanoparticle, namely $n$. We find that, as $h$ changes from 0.03 nm to 0.10 nm, correspondingly, $n$ increases from $1.8\times10^4$ to $3.5\times10^4$, while $\Phi_c$ and $H_c$ remain unchanged. Therefore, we propose that a material condensation process must happen during the growth of the nanoparticles.

From the AFM image (inset) in Fig. 4, we find that the sample with $h = 2.00$ nm is a continuous thin film and the mean diameter of the nanoparticles $\Phi_c = 26.9 \pm 4.1$ nm, indicating the contractive behavior of the nanoparticle diameter. If we assume that the shape and overlap features of the nanoparticles for all the samples are similar, then we may obtain $n = 1.3 \times 10^5$ for the sample with $h = 2.00$ nm. This result again suggests that the material condensation process really happens as the nominal film thickness increases.

During deposition, the deposited Fe atoms diffuse and nucleate on the liquid surfaces and then form unstable nanoparticles. Aggregating with other atoms and small nanoparticles, the nanoparticles grow up gradually. Meanwhile, due to the nearly free sustained surface effect, a large amount of defects and vacancies may exist and their evolution may result in the rearrangement of the microstructure and condensation of the material density inside the nanoparticles.[13] Therefore, the critical sizes of $\Phi_c$ and $H_c$ should be related to the characteristic properties of the liquid substrate effort and the microstructure of the nanoparticles. The stable microstructure of the nanoparticles may also be determined by the vacancy mechanism, microstructure, interconnections between the Fe atoms and the silicone oil molecules, etc.[21]

According to the discussion above, as the nominal film thickness $h$ increases, the mean diameter and height of the nanoparticles remain unchanged and the overlap among the nanoparticles can be neglected after the formation of the nanoparticles with critical sizes. Therefore, based on the conservation of the total numbers of the Fe atoms deposited on liquid surfaces, we obtain

$$N_0 S f \,\mathrm{d}t = N\,\mathrm{d}n + n\,\mathrm{d}N = \frac{1}{K_1}(\rho\,\mathrm{d}n + n\,\mathrm{d}\rho), \qquad (1)$$

where $N_0$ is the number of atoms per unit volume in the Fe crystal, $S$ is the sample area, $N$ is the total number of the nanoparticles, $K_1 = \pi\Phi_c^2/(4S)$ is a constant. According to our previous work,[27] the behavior of the apparent Fe coverage $\rho$ shown in Fig. 2 may be represented as $\rho = 1 - \mathrm{e}^{-Kh}$, where $h = ft$ and $K$ can be considered as a constant for $\rho \ll 1$. There-

fore, equation (1) reads

$$f\,\mathrm{d}t = \frac{1}{N_0 S K_1}[(1-\mathrm{e}^{-Kft})\,\mathrm{d}n + nkf\,\mathrm{e}^{-Kft}\,\mathrm{d}t]. \tag{2}$$

Then integrating Eq. (2) yields

$$n = \frac{\pi\Phi_c^2 N_0 ft}{4(1-\mathrm{e}^{-Kft})}. \tag{3}$$

In the early period after the nanoparticles with the critical sizes form, i.e., for $Kft \ll 1$, equation (3) may be simplified as

$$n \approx \frac{\pi\Phi_c^2 N_0}{4K}. \tag{4}$$

Equation (4) shows that, at the initial stage, the microstructure of the nanoparticles is relatively stable. However, as the nominal film thickness $h$ increases, i.e., as the deposition time $t$ goes on, equation (3) shows that the total number of Fe atoms in each nanoparticle increases, indicating that a material condensation process really occurs during this evolution period. This result is in good agreement with the experimental findings above.

## 4. Conclusions

In conclusion, branched iron aggregates are successfully prepared on silicone oil surfaces and the formation mechanism of the aggregates can be traced to the two-stage growth model. The morphology evolution from the branched aggregates to a continuous thin film is observed as the nominal film thickness $h$ increases. The high resolution AFM images show that the aggregates are composed of numerous disk-shaped nanoparticles with the mean diameter $\Phi_c \approx 31.7$ nm and height $H_c \approx 4.5$ nm. As $h$ changes from 0.03 nm to 2.00 nm, the experiment shows that both $\Phi_c$ and $H_c$ are independent of $h$, indicating that a material condensation process actually occurs during the growth period. Our theoretical result is in agreement with the experimental findings.

It is realized that the morphology and microstructure of metallic nanostructures formed on liquid substrates may evolve with time after deposition.[25,27] Since the physical properties are mainly determined by the geometric shape, the average size, the microstructure, and the stability of the nanoparticles, to systematically study the physical mechanism of the material condensation process is meaningful. Unfortunately, the detailed microstructural evolution of the nanoparticles cannot be directly measured for two reasons: (i) after the nanoparticles form on the liquid substrate, they may diffuse with a large diffusion coefficient[9] and (ii) it is believed that the material condensation process occurs during and after the deposition. Therefore, it is quite difficult for us to trace the evolution of the microstructure timely and exactly in experiment at the moment. We suggest that, in order to quantitatively study the detail formation mechanism of the nanoparticles, further efforts are still necessary.

## References


[1] Bromann K, Félix C, Brune H, Harbich W, Monot R, Buttet J and Kern K 1996 *Science* **274** 956
[2] Chopra N G, Benedict L X, Crespi V H, Cohen M L, Louie S G and Zettl A 1995 *Nature* **377** 135
[3] Shimizu T, Haruyama J, Marcano D C, Kosinkin D V, Tour J M, Hirose K and Suenaga K 2011 *Nature Nanotech.* **6** 45
[4] Zuo J M and Li B Q 2002 *Phys. Rev. Lett.* **88** 255502
[5] Tang D S, Zhou W Y, Ci L J, Yan X Q, Yuan H J, Zhou Z P, Liang Y X, Liu D F and Liu W 2002 *Chin. Phys. B* **11** 496
[6] Shi J, Votruba A R, Farokhzad O C and Langer R 2010 *Nano Lett.* **10** 3223
[7] Mu Y, Liang H, Hu J, Jiang L and Wan L 2005 *J. Phys. Chem. B* **109** 22212
[8] Amali A J and Rana R K 2008 *Chem. Commun.* 4165
[9] Ye G X, Michely T, Weidenhof V, Friedrich I and Wuttig M 1998 *Phys. Rev. Lett.* **81** 622
[10] Torimoto T, Tsuda T, Okazaki K and Kuwabata S 2010 *Adv. Mater.* **22** 1196
[11] Dupont J and Scholten J D 2010 *Chem. Soc. Rev.* **39** 1780
[12] Yu S J, Zhang Y J, Ye Q L, Cai P G, Tang X W and Ye G X 2003 *Phys. Rev. B* **68** 193403
[13] Zhang X F, Zhang C H, Lv N, Xie J P and Ye G X 2010 *Chin. Phys. Lett.* **27** 096102
[14] Gorth D J, Rand D M and Webster T J 2011 *Int. J. Nanomed.* **6** 343
[15] Jiang J, Oberdörster G, Elder A, Gelein R, Mercer P and Biswas P 2008 *Nanotoxicology* **2** 33
[16] Chen Y, Zhang Y, Birch D J S and Barnard A S 2012 *Nanoscale* **4** 5017
[17] Parent L R, Robinson D B, Woehl T J, Ristenpart W D, Evans J E, Browning N D and Arslan I 2012 *ACS Nano* **6** 3589
[18] Woehl T J, Evans J E, Arslan I, Ristenpart W D and Browning N D 2012 *ACS Nano* **6** 8599
[19] Imanishi A, Gonsui S, Tsuda T, Kuwabata S and Fukui K 2011 *Phys. Chem. Chem. Phys.* **13** 14823
[20] Kameyama T, Ohno Y, Kurimoto T, Okazaki K, Uematsu T, Kuwabata S and Torimoto T 2010 *Phys. Chem. Chem. Phys.* **12** 1804
[21] Khatri O P, Adachi K, Murase K, Okazaki K, Torimoto T, Tanaka N, Kuwabata S and Sugimura H 2008 *Langmuir* **24** 7785
[22] Ye Q L, Xu X J, Cai P G, Xia A G and Ye G X 2003 *Phys. Lett. A* **318** 457
[23] Fang Z N, Yang B, Chen M G, Zhang C H, Xie J P and Ye G X 2009 *Thin Solid Films* **517** 3408
[24] Zhang C H, Lv N, Zhang X F, Ajeeb S, Xia A G and Ye G X 2011 *Chin. Phys. B* **20** 066103
[25] Zhang C, Lv N, Zhu Y, Zhang X and Ye G 2012 *J. Phys. Soc. Jpn.* **81** 034602
[26] Chen M G, Yu S J, Feng Y X, Jiao Z W, Yu M Z and Yang B 2010 *Thin Solid Films* **518** 2674
[27] Zhang X, Zhang C, Yang B, Lv N, Pan Q and Ye G 2011 *J. Phys. Soc. Jpn.* **80** 104603