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Fast Surface Diffusion of Large Disk-Shaped Nanocrystal Aggregates

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ABSTRACT

The diffusion of planar aggregates of passivated CdSe nanocrystals on a graphite surface is investigated using AFM. These monolayer disks contain 80–100 identical 4 nm nanocrystals, with a total molecular weight of 4 × 10^7 amu, and yet diffuse rapidly on a graphite surface at 50–100 °C without dissociation. The distribution function of displacements of the disks supports the collective slip-diffusion mechanism proposed recently for single nanocrystals. The diffusion is observed to be sublinear with time, which is attributed to continuing loss of capping organic molecules from nanocrystals.

Introduction. Nanometer-sized crystallites have been a topic of active research effort in the past decade, mostly because of their size-dependent optical and electronic properties.[1] Self-assembly of these nanocrystals as "building blocks" is a promising method of creating new electronic materials, because the morphology and surface composition of the nanocrystals can be precisely controlled. In this process one important aspect is the motion of single nanoparticles. It has been recently demonstrated that single nanometer-sized bare Sb and Au crystallites containing hundreds to thousands of atoms (molecular weight 3 × 10^4 to 3 × 10^5 amu) can diffuse rapidly on a graphite surface at room temperature.[2−4] The ramified aggregate structures observed are compared to predictions of computer simulations based on a diffusion-limited aggregation model, and a diffusion constant of 10^{-8} cm^2/s for Sb_{2300} at room temperature was inferred.[2b] The diffusion mechanism is assumed to be a collective slip-diffusion: occasionally, when the collective vibration of the nanocrystals exceeds the local friction, the nanocrystals perform a long gliding slip until the kinetic energy is dissipated.[5,6] They then undergo localized vibration until the next flight. As a consequence, the probability of jumping length will be a bimodal distribution that is composed of "sticking" and "flight". The flight length step size shows a wide distribution, compared to the nearest-neighbor jumping of classical atomic diffusion on a crystal surface. This type of motion should occur on a flat surface that does not have a significant lateral corrugation. Understanding this abnormal diffusion has both fundamental and technological importance. It helps to elucidate the surface interactions, such as friction and lubrication, at the atomic and molecular level. On the other hand, it can be a potential route for making nanostructured materials by controlling postdeposition diffusion and subsequent aggregation. Different morphologies have formed by adjusting deposition flux and surface temperature.[2]

These indirect observations, albeit quite useful, are still model dependent. A diffusion constant is inferred, not measured. We report here our "freeze-and-look" AFM observations of large islands diffusing on a HOPG surface. These large species contain 80−100 CdSe nanocrystals, held together by the inherent van der Waals attraction. Each nanocrystal contains thousands of atoms. They can move on graphite because the capping molecules provide effective lubricant between the nanocrystals and the surface. In fact, at room-temperature single nanocrystals move too fast to be studied by our technique.

Experiments. CdSe nanocrystals with diameters of 4 nm are synthesized using an organometallic method.[7] These nearly monodispersed nanoparticles are passivated with a layer of trioctylphosphine oxide (TOPO) and can be dissolved in nonpolar solvents. Monolayer disk aggregates containing 80−100 CdSe nanocrystals form on graphite surfaces during spin coating of dilute nanocrystal solution in chloroform. The number density and average size of the aggregates can be varied by controlling the concentration of the solution and the spin speed (typically 2000 rpm). Tapping mode AFM (Digital Instruments, Nanoscope III) images are taken to record the initial positions of the aggregates. The sample is then subject to heating in air at the desired temperature for the desired duration. At the end of heating, the sample is quickly removed from the oven and put into a −10 °C freezer to quench the temperature. AFM images are then taken on the same area for the displacement measurement. We usually choose an area that has distinct features, such as a step edge at the corner, so that we can recognize the initial area. Island formation and diffusion are only

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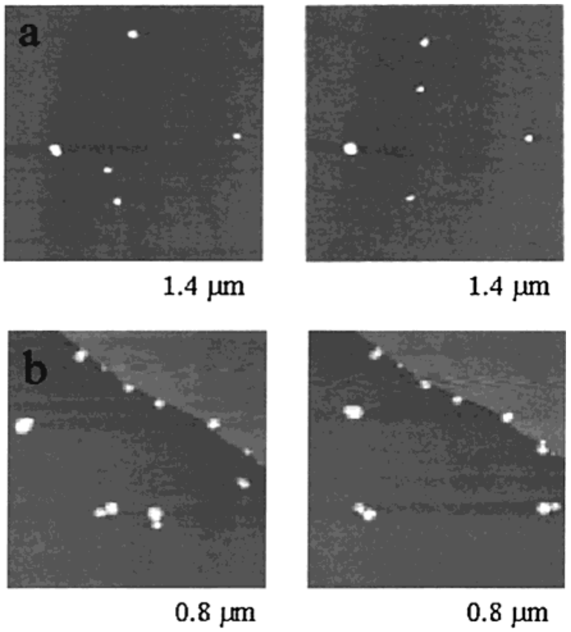

Figure 1. Ambient Tapping mode AFM image (scan rate 1 Hz) of the same area before and after heating. Islands trapped at a step edge do not move.

observable on graphite. On mica and silicon oxide nanocrystal aggregation is hindered; only single nanoparticles are observable. They do not show any evidence of motion even when heated to 120 °C for hours.

Results and Discussion. Compact round disks of nanocrystals form spontaneously after spin coating a drop of dilute nanocrystal solution on graphite. Their formation has been modeled as a gas−liquid phase separation in a 2-D van der Waals system.[8] During drying the concentration of nanocrystals in the solution increases, and at the same time nanocrystals experience stronger attraction due to reduced screening of the van der Waals force between each other. Homogeneous nucleation happens as the result, which generates the observed disks. The disks are a monolayer thick due to the strong wetting of nanocrystals onto graphite. The surface coverage is adjusted to less than 5%, and the number density to approximately five islands per micrometer. Disks formed have a relatively narrow size distribution. Generally, the number of disks is increased when the concentration of the nanocrystal solution is larger, whereas their diameter is increased when the spin speed is smaller. The aggregates have more time to grow because the drying is slower with smaller spin speed. We choose the size of the disks to be ~50 nm in diameter because smaller disks are easier to be dragged by AFM tip and do not give stable images.

Figure 1 illustrates the AFM image of one area before and after heating at 90 °C for 4 min; One disk has moved about 500 nm. The disks do not change shape significantly during moving. This enables us to distinguish individual aggregates and measure their displacement. We have never observed any disk dissociation during motion. The bonding between nanocrystals must be much larger than KT in these dry disks.[8] Note in (b) the dimer-like islands formed by two disks attached to each other. They performed translation as well as rotation without merging into one disk. This pivoted slip happens when the disk experiences a torsion. These observations clearly show that the disks move as units. Statistics on the self-rotation angle, and the direction for single disks, shows isotropic behavior. Also, there is no observable correlation between contingent displacements. The former motion does not affect later ones.

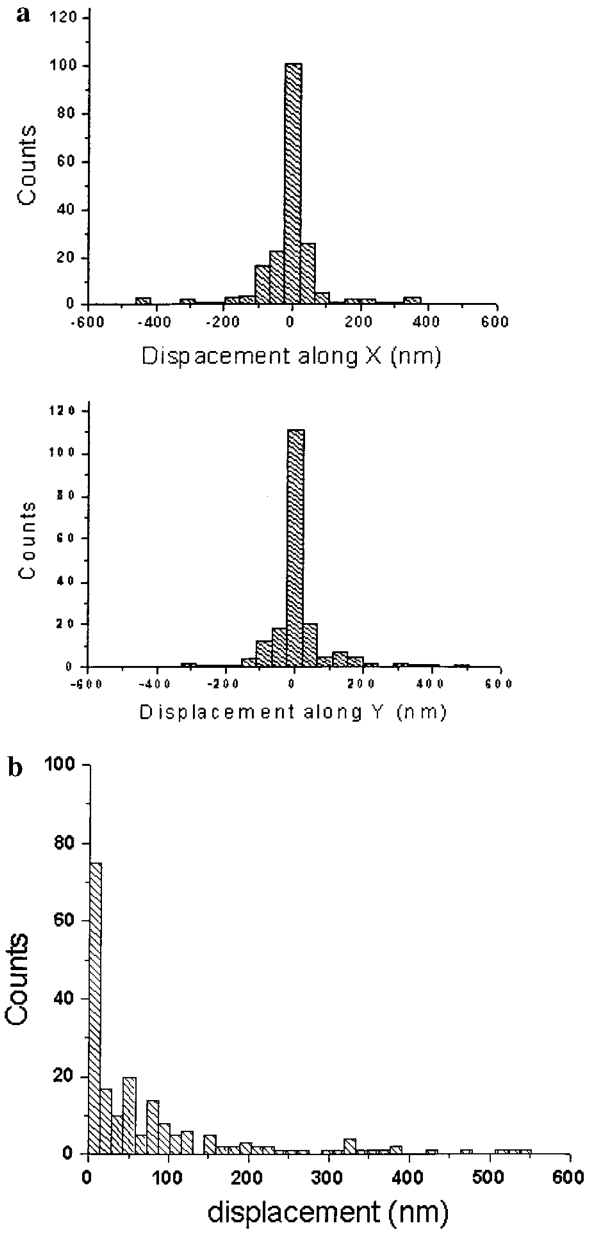

Figure 2. (a) Displacement distribution for X and Y motion from measurements of one time step for 200 islands. The sample was heated at 95 °C for 5 min. (b) Distribution of the displacement length from (a).

Figure 2 shows the displacement distribution from a single time step at 95 °C. The distribution in (a) is far from a Gaussian form. However, if we increase the heating time, the distribution approaches a Gaussian (data not shown). This indicates that in the 5 min of heating, particle islands performed a few random glide steps and have not reached the Gaussian form mathematically expected after 10 jumping steps in a simple diffusion model.[9] In the Leutdke and

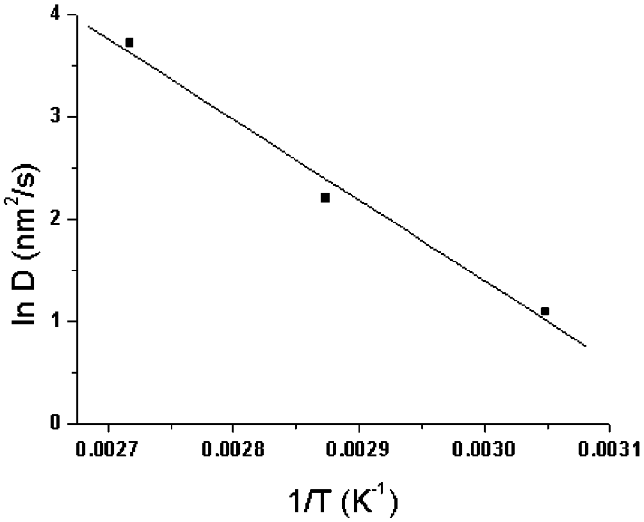

Figure 3. Temperature dependence of diffusion constant and the Arrhenius-form fit. Experiments were done at 55, 75, and 95 °C for intervals of 5−10 min.

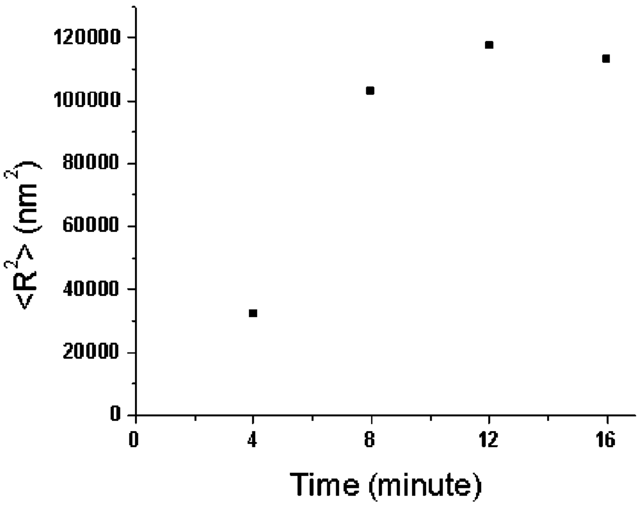

Figure 4. Time dependence of ensemble average of $\langle R^2 \rangle$. One sample was heated at 90 °C for successive periods of 4 min.

Landmann (LL) computer simulations for single Au nanocrystals,[6] random glide steps occurred on a nanosecond scale and the typical length is 3−4 Å. Larger aggregates should perform slip motion much less frequently and with long slip lengths.

The distribution of displacement length in Figure 2b shows a wide, continuous distribution, ranging from 0 to 500 nm. Because this 5 min diffusion is still in the early time limit (less than 5 steps), the broad distribution will keep the shape of the original single-step jumping distance distribution. This agrees with the computer simulation by LL on a single nanocrystal without organic lubricant on HOPG.[6] Intuitively, the initial velocity and subsequent slip length might show a Maxwell distribution above some cutoff values. We also observed that the ratio between sticking and flight is a function of temperature. With higher temperature, disks spend less time in the local potential well and perform flights more frequently. Alternatively, LL observed a power-law decay of the length distribution in their simulation, which is characteristic of the Levy flight mechanism. Statistics are not sufficiently precise to determine this point in our experiment.

An effective diffusion constant can be obtained by $\langle R^2 \rangle = 4Dt$, even if the distribution of R is not Gaussian. We plot in Figure 3 the temperature dependence of D and the Arrhenius fit assuming $D = D_0 \exp(-E_a/\mathrm{KT})$. The activation energy per disks is 0.7 eV and $D_0 = 7 \times 10^{10}$ nm^2/s. This small activation energy reflects the lubrication by the organic capping molecules. This is in agreement with the computer simulation in ref 5 where for a single Au nanocrystal with a C_{12} thiol capping to slip, a critical shear stress has to be overcome by the vibrational energy of 0.017 eV. For Au nanocrystals with C_4 thiol capping, this activation energy is 0.007 eV. Our disk aggregates have areas roughly 100 times that of single nanocrystals. However, the effect of temperature on the conformation of capping molecules, and thus on the prefactor D_0, are still not known.

The diffusion constant for disks with diameters of 50 nm in our temperature ranges are from 3 to 60 nm^2/s, compared with ∼100 nm^2/s of spheres with the same diameter in liquid hexane and ∼5000 nm^2/s in air, calculated from Stokes−Einstein law. Amazingly, D is not much smaller than expected in liquid hexane.

Figure 4 shows the averaged $\langle R^2 \rangle$ as a function of time from an ensemble of 30 islands, for a series of 4 min steps. $\langle R^2 \rangle$ follows the well-known linear relation until around 10 min. After that the diffusion gets slower and eventually the islands stop moving. As they slow, we observe growth of patches of molecules around these islands, with heights ∼0.6 nm. We believe they are TOPO molecules desorbed off the CdSe nanocrystals by heating. This reduces the distance between nanocrystals and the surface and increases the static friction around the nanocrystal islands, eventually stopping their motion. Desorption of capping molecules from gold nanocrystals has been observed experimentally starting from 75 °C.[10,11] This could be enhanced in our system due to the van der Waals interaction between TOPO molecules with graphite and relatively weaker bonding between O atoms and Cd atoms. As another illustration, the experiment of Figure 2 was done on a sample that was inspected for 2 weeks before heating. During this time the TOPO molecules slowly come off the nanocrystals and migrate onto graphite. As a consequence, the diffusion constant measured is 20 nm^2/s, about half that expected from Figure 3.

We have never observed single nanoparticles on graphite. They must either be swept by the AFM tip or move between aggregates faster than the scanning rate. This gives a lower limit of $D = 10^6$ nm^2/s for single particles (assuming a 1 μm scan at scan speed of 1 Hz). With solvent still present, this diffusion will be even faster. The self-assembly of nanocrystals is often interpreted as an equilibrium and adiabatic phase separation process. This model is supported by our observations.

Although we observed that large islands move slower than smaller islands, accurate size-dependent diffusion constant cannot be gained due to the difficulty of determining the island size. Capping molecules desorb from nanocrystals constantly. As a result, the local friction around islands may differ from sample to sample and slowly increases with time. More work is needed to fully quantify aspects of this diffusion process.

Conclusion. Large aggregates containing up to 100 nanocrystals are found to diffuse ∼100 nm on a graphite surface upon mild heating. The diffusion constant decreases with time while the friction increases. These large species spend most of the time sitting in their local potential well, only performing a few random glide steps per minute.

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Note Added in Proof. For reviews on Levy statistics, please see: Shlesinger, M. F.; Zaslavsky, G. M.; Klafter, J. *Nature* **1993**, *363*, 31. Klafter, J.; Zumofen, G. *Phys. Rev. B* **1994**, *49*, 4873.

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