Nucleation and Growth of the Prototype Azabenzene 1,3,5-Triazine on Graphite Surfaces at Low Temperatures

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ABSTRACT: We report on research performed by using scanning tunneling microscopy (STM) during the first stages of nucleation and growth of a prototype azabenzene, 1,3,5-triazine, on highly oriented pyrolitic graphite (HOPG) surfaces at low temperatures under ultrahigh vacuum conditions. This work reveals the formation at temperatures below 100 K of two-dimensional fractal shape islands of 1,3,5-triazine where the molecules are ordered in an hexagonal lattice. By using nucleation theory on well-controlled experiments, where sample temperature and deposition rate were alternatively changed, we have extracted important parameters such as the critical nucleus size (equal to one) and the energy barrier for single molecule diffusion ($E_d = 55 \pm 8$ meV). This energy barrier, though low enough to be considered the result of a weak molecule–substrate interaction corresponding to a physisorption process, is much higher than the one obtained very recently for the benzene–graphite system [Hedgeland, H.; et al. Nat. Phys. 2009, 5, 561]. This comparison suggests that the presence of the nitrogen atoms on the heterocycle of azabenzenes can lead to a substantial gain on the bonding energy with respect to pure benzenic systems.

INTRODUCTION

Graphite has been considered a prototype surface for the growth of well-ordered self-assembled molecular layers, mainly due to a reduced substrate–molecule interaction as compared to typical intermolecular interactions on surfaces. In the last few years the study of the adsorption and initial stages of growth of molecular layers on these surfaces has gained renewed interest as graphene-like materials are attracting extraordinary attention both from fundamental and applied viewpoints. For instance, the growth of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) has been studied comparatively on highly oriented pyrolitic graphite (HOPG) and on epitaxial graphene on SiC surfaces, outlining some similarities and differences for the growth on each of these two substrates. Thus, some of the conclusions drawn from adsorption and growth studies on HOPG can probably be transferred to epitaxial graphene surfaces. There is, however, an urgent need of quantitative information on the diffusion and growth at the initial stages, that is, below the completion of the first ordered layer, of aromatic molecules on graphite or graphene-type systems. Hedgeland et al. have very recently presented a combined experimental and theoretical study of the diffusion of benzene on HOPG surfaces. According to their study, the diffusion barrier for this system is so low ($17 \pm 12$ meV) as to be considered an anomalous atomic-scale continuous Brownian motion of the diffusing species.

In the present work, we have analyzed the initial stages of nucleation and growth of a prototype azabenzene molecule on HOPG surfaces by means of variable-temperature scanning tunneling microscopy (STM). The molecule of choice has been 1,3,5-triazine—also denoted sym-triazine or s-triazine (see Figure 1a)—a very simple aromatic molecule incorporating three N atoms, which can allow one to test the influence of the corresponding lone pairs on the surface diffusion on a rather inert surface such as HOPG. STM has been used successfully in the past for the extraction of nucleation and diffusion parameters on the growth of adatoms on both metal and semiconductor surfaces. There are, however, scarce examples of the application of quantitative nucleation theory on STM data of organic molecule growth on surfaces. Here, we present quantitative data deduced from STM measurements of 1,3,5-triazine on HOPG performed under ultrahigh vacuum (UHV) and at sample temperatures below 100 K. Our results show that the diffusion barrier for this prototype azabenzene molecule is highly enhanced with respect to the corresponding benzene molecule.

The paper is structured as follows. After this introduction, the experimental details on the preparation of the samples and on the STM measurements are given. The results on the initial stages of adsorption of 1,3,5-triazine on HOPG surfaces are then presented. The application of nucleation theory on STM data leads to the experimental extraction of the critical nucleus as well as the diffusion barrier for single molecules. These results are discussed in comparison to previous reports on diffusion of benzene on HOPG.

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**EXPERIMENTAL METHODS**

The experiments were performed in an ultrahigh vacuum system with a base pressure of $10^{-10}$ Torr equipped with a home-built variable temperature scanning tunneling microscope (VT-STM). A modified version of the microscope described in ref 22 was used. The cooling down of the sample was performed by using a liquid helium continuous flow cryostat with a heater attached that allows control of the sample temperature through a feedback loop. The operation range of this VT-STM is from 40 to 400 K. The tips were made out of electrochemically etched tungsten; they were cleaned in situ, in UHV, by high-temperature annealing and field emission against a Ta electrode. HOPG samples were cleaved in situ by means of a homemade device specifically designed for this purpose. As a result, surfaces with large and clean terraces of more than 500 $\times$ 500 nm$^2$ were routinely obtained. In order to deposit the s-triazine (Sigma-Aldrich, 97% purity) on the graphite surface under optimal conditions, it was necessary to clean the glass container of the s-triazine molecules by using repeated freeze—pump—thaw cycles. Afterward, the s-triazine was sublimated from the glass container filling the whole UHV system by means of a leak valve, until a stable pressure of $10^{-8} - 10^{-9}$ Torr was reached, while our freshly cleaved HOPG substrate was kept at the desired temperature in the range of 40—90 K. By fine-tuning the partial pressure and the time, the triazine exposure could be changed, leading to the desired deposition rate and coverage. Typically one-third of a monolayer (ML) was deposited by means of 3 langmuir exposure. One ML is defined with respect to the saturation coverage for the self-assembled hexagonal lattice of molecules described below and not with respect to the substrate surface density. It corresponds to $3.1 \times 10^{14}$ molecules/cm$^2$. After the sublimation, the temperature of the sample was quenched to 40 K in order to avoid further motion of the molecules induced by the tip during the STM scanning. All data acquisition and image processing was performed using the WSxM software.$^{23}$

**RESULTS AND DISCUSSION**

**Adsorption of 1,3,5-Triazine.** As shown in Figure 1, the exposure of the graphite surface at temperatures between 40 and...
90 K to s-triazine for coverages below one monolayer resulted in the formation of highly ramified, fractal, or dendritic-type, two-dimensional islands. Fractal patterns in nature are often related to growth processes far from equilibrium. STM has been used to characterize fractal and self-affine surfaces since the initial years of the technique. Two dimensional fractal or dendritic islands were also observed with STM some time ago, in the first stages of growth of inorganic materials on metal or semiconductor surfaces. Much more recently, they have been also observed on the growth of some molecules on surfaces. These highly ramified self-similar two-dimensional islands are usually associated with the DLA (diffusion limited aggregation) model proposed by Witten and Sanders. In the present case, the overall shape of the 1,3,5-triazine islands is consistent with the growth conditions at low temperature.

Figure 1d shows an STM image of an area of $83 \times 83$ nm$^2$ where one such fractal island formed after the adsorption of $1/3$ ML of s-triazine on the graphite surface at 58 K is imaged. A profile across the fractal islands along the blue line marked in the left part of that image is shown in Figure 1f. Although electronic effects can be convoluted to topography in STM images, the apparent island height is close to 2 Å, which is a strong indication that the fractal islands correspond to monolayer islands (and not to multilayers). Moreover, Figure 1e displays a higher resolution STM image of the $5 \times 4$ nm$^2$ area, marked with a rectangle in Figure 1d, just inside one of the branches of the island, where it is observed that such islands are composed of bright protrusions ordered in a hexagonal lattice with a lattice parameter of 6.1 Å. Similar arrays with a flat orientation have been proposed in the adsorption of s-triazine and other simple azabenzeno molecules physisorbed via the weak interaction of the molecular orbitals $\pi$ ring with other noble metal surfaces. In the present experiments, although a long-range order is observed in the islands, there are a high number of defects. This order can be improved either by increasing the sample temperature at around 150 K after the deposition or by depositing the s-triazine onto the substrate at 150 K. Such conditions result in large islands of s-triazine with the molecules exhibiting a perfect ordered structure in a hexagonal lattice with a lattice parameter of 6.1 Å.

Figure 2. 500 × 500 nm$^2$ STM images of s-triazine islands on HOPG after deposition of 0.33 ML of s-triazine at $T = 43$ K and at different rates ($F$): (a) $F = 1.7 \times 10^{-5}$ molec·Å$^{-2}·s^{-1}$; tunneling parameters, $V_S = 3.6$ V, $I_T = 27$ pA; (b) $F = 1.0 \times 10^{-5}$ molec·Å$^{-2}·s^{-1}$; tunneling parameters, $V_S = 3.3$ V, $I_T = 30$ pA; (c) $F = 4.4 \times 10^{-6}$ molec·Å$^{-2}·s^{-1}$; tunneling parameters, $V_S = 3.6$ V, $I_T = 18$ pA. (d) Plot of the island densities versus the deposition rate $F$. From the slope we obtain $\chi = 0.3 \pm 0.1$, close to 0.33 corresponding to a critical nucleus equal to 1.
Nucleation of 1,3,5-Triazine Islands on the HOPG Surface.

Once the s-triazine molecules have been adsorbed onto the HOPG surface, they start diffusing among different adsorption sites. This movement of the molecules over the surface in a random walk stops when one molecule finds another, giving rise to a cluster or island. Islands with a number of molecules below a certain value, known as the critical nucleus, can decay through detachment of molecules from the islands. These processes are described by nucleation theory. According to this theory, an exponential dependence between the island’s density and the substrate temperature, as well as a power law dependence of the island’s density with the deposition rate, can be found as outlined by the following expression:  

\[ N_i = \frac{a^4 \Omega^2 F}{\nu_0^2} \exp \left[ \frac{E_i + iE_d}{(i + 2)kT} \right] \exp \left( \frac{E_i + iE_d}{i + 2} \right) \]

where \( i \) is the critical nucleus defined as the minimum number of molecules in a stable cluster, \( \langle N \rangle \) is the average number of islands per adsorption site, \( F \) is the deposition rate, \( \nu_0 \) is the attempt frequency, \( E_i \) is the binding energy of the cluster corresponding to the critical nucleus, \( E_d \) is the barrier for single molecules diffusion, \( T \) is the temperature of the substrate, \( \Omega \) is the area of the molecular unit cell, \( a \) is the lattice parameter of the substrate unit cell, and \( \chi = i/(i + 2) \). The dimensionless parameter \( \eta \) depends on the coverage and is usually taken as a constant equal to 0.25 (see refs 16, 32).

a. Critical Nucleus Determination. The first stage, in order to apply the nucleation and growth theory, is to determine the critical nucleus size. Through the power law dependence between the island density and the rate, the critical nucleus size can be determined by means of experiments consisting of depositing the same amount of s-triazine at different deposition rates over the graphite substrate at a fixed temperature. It is important to note that the critical nucleus size is, in general, temperature dependent, and for this reason these experiments must be performed with the substrate at temperatures inside the range at which we will develop the experiments described in the next section. In Figure 2a–c, we can see STM images acquired onto equal areas of 500 × 500 nm² after the deposition of 1/3 ML of s-triazine molecules at different deposition rates over the graphite substrate at a fixed temperature. It is possible to observe how the number of islands increases by increasing the deposition rate. Then, by plotting the island density versus the deposition rate \( F \) just as shown in Figure 2d and using eq 1, we can extract from the slope a value \( \chi = 0.3 \pm 0.1 \). This value is in good agreement with the expected
value $\chi = 1/3$ for a critical nucleus size equal to 1. This means that dimers of molecules are stable and they do not diffuse. It is interesting to compare this fact with the result reported by Kim et al. that dimers of nitrogen atoms in the benzene ring are very stable via the formation of two hydrogen bonds $\text{C}^+\cdot\cdot\cdot\text{H} \cdots \text{N}$ between them.

b. Diffusion Barrier and Attempt Frequency Determination. Because of the exponential dependence between the island density and the substrate temperature indicated in eq 1, an Arrhenius plot of $\ln(D)$ versus $1/T$ should give us the values for the diffusion barrier and the attempt frequency. Figure 3 shows STM images acquired onto areas of 500 $\times$ C2 the diffusion barrier and the attempt frequency. Figure 3 shows an increase of the diffusion barrier of single $s$-triazine molecules on graphite surfaces at low temperatures by means of variable temperature scanning tunneling microscopy. We have found that the $s$-triazine molecules are arranged in a hexagonal lattice with 6.1 Å periodicity forming fractal–dendritic shape islands. From nucleation experiments consisting of changing the deposition rate for fixed coverage and graphite temperature, we observe the critical nucleus to be equal to 1, which means that $s$-triazine dimers are stable. By means of experiments in which we sublimate the $s$-triazine at a fixed coverage and rate for different graphite temperatures, a value of 55 ± 8 meV is extracted for the diffusion barrier of single $s$-triazine molecules on graphite surfaces. The low diffusion barrier is indicative of a weak molecule–graphite interaction. However, the comparison of these results with the adsorption of benzene on a graphite surface, where much lower diffusion barriers have been reported, suggests that the substitution of the three carbon atoms for three nitrogen atoms in the benzene ring could be responsible for the increase of the diffusion barrier observed. This is consistent with the picture of a strong bonding with the graphite surface, in agreement with DFT calculations that have been reported for the adsorption of $s$-triazine on graphene.

**REFERENCES**


**CONCLUSIONS**

We have studied the growth within the submonolayer regime of $s$-triazine on graphite surfaces at low temperatures by means of variable temperature scanning tunneling microscopy. We have found that the $s$-triazine molecules are arranged in a hexagonal lattice with 6.1 Å periodicity forming fractal–dendritic shape islands. From nucleation experiments consisting of changing the deposition rate for fixed coverage and graphite temperature, we observe the critical nucleus to be equal to 1, which means that $s$-triazine dimers are stable. By means of experiments in which we sublimate the $s$-triazine at a fixed coverage and rate for different graphite temperatures, a value of 55 ± 8 meV is extracted for the diffusion barrier of single $s$-triazine molecules on graphite surfaces. The low diffusion barrier is indicative of a weak molecule–graphite interaction. However, the comparison of these results with the adsorption of benzene on a graphite surface, where much lower diffusion barriers have been reported, suggests that the substitution of the three carbon atoms for three nitrogen atoms in the benzene ring could be responsible for the increase of the diffusion barrier observed. This is consistent with the picture of a stronger bonding with the graphite surface, in agreement with DFT calculations that have been reported for the adsorption of $s$-triazine on graphene.

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