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Haeckelite and graphene formation on a metal surface: Evidence for a phase transition at the edge of criticality

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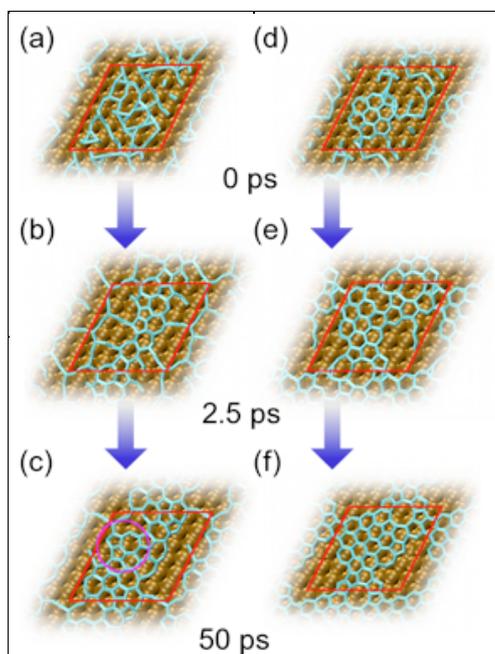


Figure 1. Snapshots of trajectories 6h (a-c, left) and 7g (d-f, right) at 0, 2.5, and 50 ps, respectively. The location of the periodic boundary is indicated by the red line. The circle in 1c) denotes an area of late ring collapse from a Y-junction.

Nosé-Hoover chain thermostat connected to the degrees of freedom of the system. The nuclear temperature was maintained at 1180 K throughout all simulations. The four-layer Ni(111) model surface used in both models consisted of 144 Ni atoms. Three-dimensional periodic boundary conditions (PBC) were enforced on this model system during all simulations. To study the nucleation of the first sp^2 carbon ring systems from sp carbon on a terrace, we selected a constant and rather large 83.3 mole% of the carbon density of a perfect, continuous sheet of graphene. In the ‘H’ set of ten trajectories, we randomly placed horizontally aligned C_2 units on a Ni(111) surface without initial polygonal order [Fig. 1(a)], much like in our study of fullerene formation [3]. In the ‘G’ set of ten different trajectories, we replaced 12 C_2 units by a domelike C_{24} carbon cluster with coronene skeleton. This served to investigate a possible template effect by its existing hexagon network. A total of 20 trajectories were computed, individually labeled as **1h-10h** and **1g-10g** for H and G cases, respectively.

Our simulations [4] clearly show that at high carbon concentration, graphene nucleation is driven by

The formation mechanism of graphene on metal surfaces is still topic of fierce debate. No reliable, real-time simulations have been reported in the literature for this phenomenon. We have therefore performed extensive quantum chemical molecular dynamics (QM/MD) simulations of graphene nucleation on a Ni(111) surface, using a modified DFTB+ program [1]. The SCC-DFTB wave function, energy and its gradient were computed ‘on-the-fly’ at each step of the dynamics. A fractional orbital occupation Fermi-Dirac distribution was employed with an electronic temperature (T_e) [2] of 3000 K. The equations of motion of nuclei were integrated using the Velocity-Verlet algorithm, with the NVT ensemble being maintained via a self-implemented

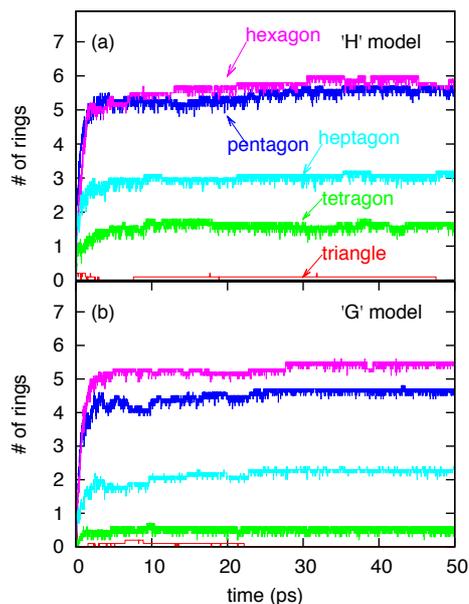


Figure 2. Average populations of newly formed carbon rings observed during 50 ps simulations.

dynamics [Fig. 1(a)]. In the case of G series trajectories, the QM/MD simulations clearly demonstrate the presence of a ‘templating effect’ of the coronene-seed on graphene nucleation, by the promotion of hexagonal ring formation at the expense of pentagons and heptagons [see Fig. 1(b) and Fig. 2]. We predict therefore that it may be possible to synthesize intrinsically metallic haeckelite by ‘shock-freezing’ at an early nucleation stage, and to promote high quality graphene growth by using hexagonal seed clusters should enhance the quality of graphene layers grown in experiment.

Furthermore, we found similarities between graphene nucleation and other critical phase transition phenomena [6]. Our analysis confirms the existence of a critical n_{C-C}/N_C value close to 1.0 (‘H’ model) and 1.1 (‘G’ model), where n_{C-C} is the number of C-C bonds and N_C is the number of carbon atoms. As in random graph theory, above this critical value, the further conversion of linear carbon chains to sp^2 carbon polygons leads to the emergence of a fully networked carbon structure. *Thus we find it justifiable to discuss the sp^2 network formation from sp chains in the context of critical phase transition phenomena [6].*

References:

- [1] Aradi, B.; Hourahine, B.; Frauenheim, T. *J. Phys. Chem. A* **2007**, *111*, 5678.
- [2] Weinert, M.; Davenport, J. W. *Phys. Rev. B* **1992**, *45*, 13709.
- [3] Irle, S.; Zheng, G.; Wang, Z.; Morokuma, K. *J. Phys. Chem. B* **2006**, 14531.
- [4] Wang, Y.; Page, A. J.; Nishimoto, Y.; Qian, H.-J.; Morokuma, K., submitted (2011).
- [5] Ohta, Y.; Okamoto, Y.; Page, A. J.; Irle, S.; Morokuma, K. *ACS Nano* **2009**, *3*, 3413.
- [6] Bak, P.; Tang, C.; Wiesenfeld, K., *Phys. Rev. Lett.* **1998**, *59*, 381.

the rapid formation of long polyyn chains, which undergo a swift phase transition resulting in a fully connected sp^2 network, according to Ostwald’s ‘rule of stages’. In the case of H series trajectories, ring nucleation begins with the formation of pentagons as a result of the dynamics of carbon Y-junctions, similar as previously described by us for the nucleation of caps on iron nanoparticles [5]. The positive curvature of the pentagons is subsequently compensated for by the condensation of heptagons, which possess negative curvature. As a result, an sp^2 network strongly resembling haeckelite (a hypothetical compound consisting only of pentagons and heptagons) emerged as a result of the