Size-Selective Carbon Nanoclusters as Precursors to the Growth of Epitaxial Graphene

Bo Wang, Marco Caffio, Renald Schaub

EaStCHEM School of Chemistry, University of St Andrews, United Kingdom

Xiufang Ma, Wei-Xue Li

Center for Theoretical and Computational Chemistry, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China
Outline

- What we know (and don’t know) about graphene formation on TM surfaces
- Ethylene/Rh(111): temperature programmed growth (TPG)
- Identification of size-selective carbon clusters as precursors: $\text{C}_{24}$
- Comparison with $\text{C}_{24}\text{H}_{12}/\text{Rh}(111)$
- Understanding the “magic” stability of $\text{C}_{24}$ from first-principles
How does graphene form on 4d & 5d TMs?

- We don’t know what are the processes that bring carbidic clusters (strongly bound) to develop into a graphene island (weakly bound)

- Graphene/TM by DFT (from Peter Feibelman’s work):
  - attachment energy of isolated C atom to graphene edge is prohibitively high, whereas it decreases significantly for larger C clusters

- Graphene/Ru(0001) by LEEM (from Kevin McCarty’s work):
  - non-linear growth kinetics strongly suggests growth by incorporation of clusters of approximately 5 C atoms rather than monomers

- Yet, these fundamental building blocks of graphene have not been formally identified

- We will perform TPG of ethylene on Rh(111)

Loginova et al., NJP 10, 093026 (2008)
Morphology evolution during TPG:
18 L of $\text{C}_2\text{H}_4$ at RT on Rh(111)

- **At 300°C:**
  - (2×2) and c(4×2) superstructures
  - ethene deprotonates to ethylidyne
  - adsorbs in 3-fold hcp hollow sites
  - C-C axis normal to the surface

- **At 500°C:**
  - small protrusions located on terraces
  - sizes from ranging from 1 to 2 nm
  - apparent height of less than 0.2 nm

- **At 600°C and above:**
  - single cluster size of 1 nm
  - decrease in the particle density
  - emergence of graphene islands
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Size-selective carbon nano-islands as precursors to graphene!
Growth mechanism: Smoluchowski ripening

- RT: adsorbed ethene $\rightarrow$ ethylidyne
- Annealing $\rightarrow$ thermal decomposition
  - structural rearrangement of C-C bonds $\rightarrow$ C2 coupling
  - dehydrogenation (C-H bond scission, H evolution)
  - in line with C$_2$H$_4$/Pt(111)
- Remarkable:
  - evolution to mono-dispersed entity
  - randomly scattered on terraces
  - no influence of step edges
  - no loss of carbon to the bulk
- Decrease in mono-dispersed clusters $\rightarrow$ graphene growth
  - not only at steps but also on terraces
- Rate determining step in graphene growth: cluster coalescence mechanism
Identification of the magic carbon clusters

- Size distribution of the carbon clusters at different temperatures reveals lower limit, or critical size:
  - diameter of 1 nm
  - nearly perfectly hexagonal in shape and adsorbed in 3-fold fcc hollow site

- thermal decomposition (dehydrogenation) of ethene is complete above 770 K:
  - most probable chemical structure: 7 honeycomb carbon units arranged in hexagon
  - from STM images at low bias: visual impression that central benzene unit lies higher than its surrounding neighbours $\rightarrow$ 2 Å high dome-shaped configuration

$7C_6$

How can we prove it?

1) Comparison with coronene
2) STS for electronic fingerprint
3) DFT support
7C₆ vs. coronene: topography

- Coronene = C₂₄H₁₂ = the hydrogenated analogue of 7C₆

- Coronene deposited at RT on Rh(111):

  ![STM topographic images](image)

  STM topographic images show (irrespective of tunnelling bias):
  - lateral size: C₂₄H₁₂ > 7C₆ in line with molecular skeleton
  - electronic height: C₂₄H₁₂ < 7C₆ by 0.5 Å
  - symmetry: 2-fold ; 3-fold different adsorption sites
7C₆ vs. coronene: electronic structure

- dl/dV spectra identify:
  - 7C₆: two resonances (HOMO+LUMO)
  - C₂₄H₁₂: single resonance (LUMO)
  - spectra are different

- dl/dV images at resonances:
  - 7C₆: 3/6-fold symmetric
  - C₂₄H₁₂: 2-fold symmetric

- 7C₆ and C₂₄H₁₂ are two different chemical entities:
  - different topographic signatures
  - different adsorption sites
  - different electronic signatures
DFT optimized structures

Predictions for $7C_6$:
- adsorbs “equally” on all registries
  $\rightarrow$ STM reveals ONLY fcc!
- dome-shaped with central benzene unit higher
- bonding to substrate mainly at peripheral C atoms

Predictions for $C_{24}H_{12}$:
- adsorption strongly favours bridge sites
- geometric height lower than $7C_6$ by 0.5-0.8 Å
- bonding to substrate shared by all C atoms

In agreement with: Lacovig et al., PRL 103 (2009)
Simulated STM images seem to confirm that the favoured adsorption site is:

- $7C_6$: 3-fold hollow site
- $C_{24}H_{12}$: 2-fold bridge site
Theoretical stability of $NC_6$ clusters

-Computed formation energy for various carbon cluster sizes (in units of benzene rings) on Rh(111)
  - $E_{C-C}$ = formation energy, free cluster
  - $E_{C-M}$ = adsorption energy
  - $E_{TOT}$ = overall energy gain
  - X axis = ratio edge C’s / total C’s

- $NC_6$ carbon cluster stability scales linearly with \( \frac{number\ of\ edge\ atoms}{total\ number\ of\ atoms} \) peripheral bonding (Lacovig et al. PRL 2009)

-$NC_6$ carbon clusters become more stable than isolated C atoms for $N=7$ !

- Stability arises from a delicate balance between C-C and C-M bond strengths
Is this particular to the G/Rh(111) system?

- Graphene growth on Ru(0001) also proceeds by via the formation of $NC_6$ precursors.

- Zangwill and Vvedensky show, on the basis of the McCarty LEEM data, that graphene islands grow by the attachment of 5C clusters, and predict that the smallest stable precursor to graphene is 6C$_5$.
Graphene growth on Rh(111) proceeds under TPG by:

- adsorption of the carbon source, dehydrogenation and coupling of $\text{C}_2$ units;
- stabilization of mono-dispersed carbon clusters: $7\text{C}_6$;
- formation by incorporation, coalescence (Smoluchowski ripening).
Those who did the work

- Research group in St Andrews, UK performed STM
  - Bo Wang
  - Marco Caffio

- Collaborators in Dalian, China performed DFT
  - Prof. Wei-Xue Li
  - Xiufang Ma

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Computational details

(Xiufang Ma, Wei-Xue Li @ Dalian, China)

- Periodic DFT calculations using VASP
  - generalized gradient approximation, PBE functional
  - PAW potentials
  - plane wave basis with 400 eV cutoff energy for geometry (electronic) calculations
  - optimization with residual forces on atoms less than 0.02 eV/Å

- Supercell
  - slab geometry composed of five metal layers with lower two kept frozen
  - vacuum region of about 15 Å,
  - for C atom adsorption: use (2×2) unit cell with (6×6×1) Monkhorst-Pack grids.
  - for C clusters: use (4×4), (6×6), (7×7) unit cell according to cluster size and use (3×3), (2×2), (1×1) Γ centered K sampling points for the BWZ.