Preparation and Application of Chemically Functionalized Graphene

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International Conference

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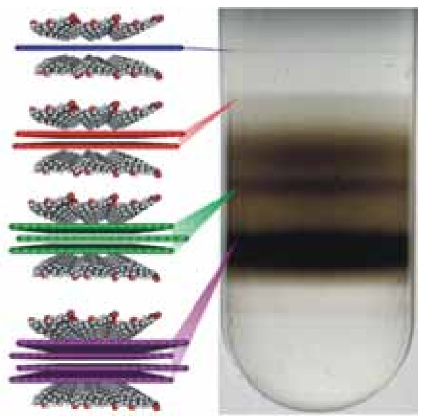
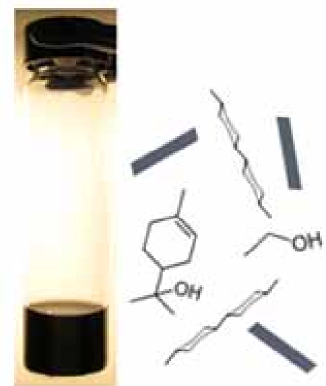
Hersam Group Graphene Research: Dispersions

Aqueous surfactant graphene dispersions



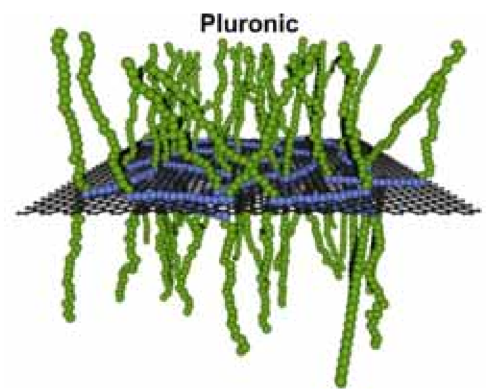
Nano Lett., **9**, 4931 (2009).

Organic solvent graphene dispersions



JACS, **132**, 17661 (2010).

Biocompatible graphene dispersions



JPCL, **2**, 1004 (2011).

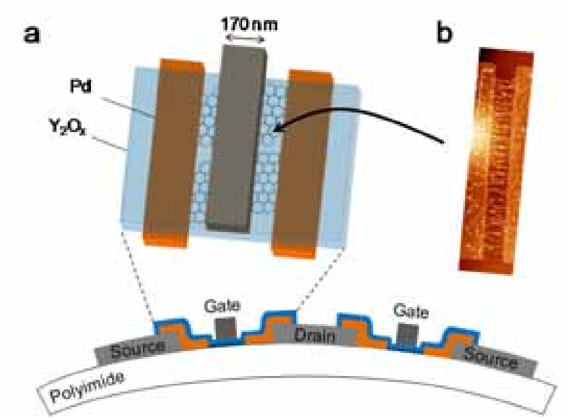
Industrial scale up and commercialization

NanoIntegris

www.nanointegris.com

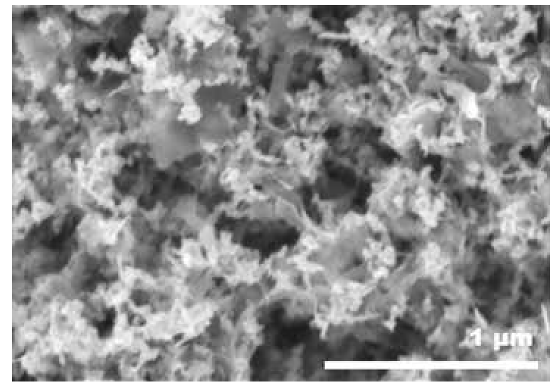
Hersam Group Graphene Research: Applications

Solution-processed GHz flexible FETs



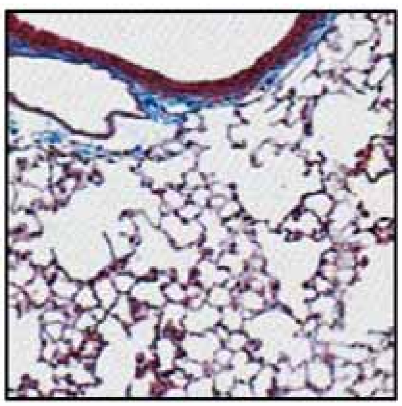
Nano Lett., **12**, 1184 (2012).

Graphene-titania photocatalysts



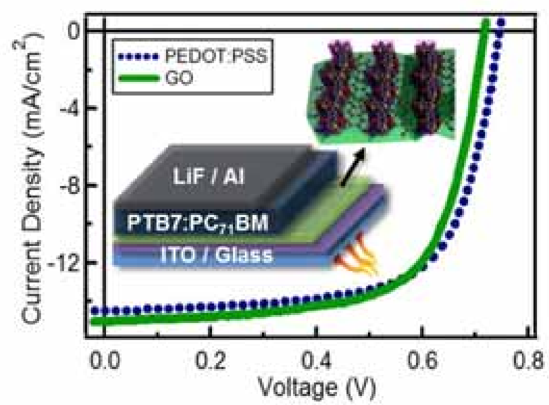
Nano Lett., **11**, 2865 (2011).

Pulmonary in vivo graphene applications



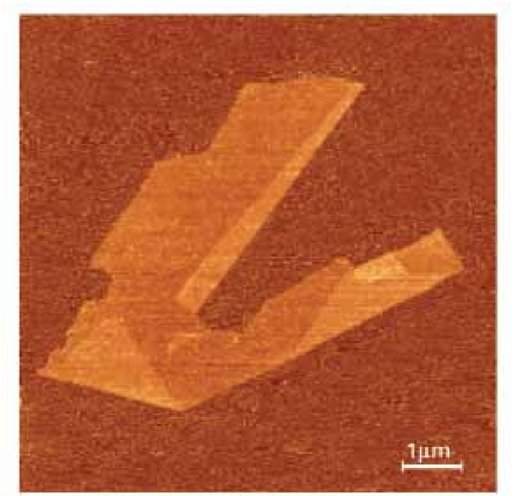
Nano Lett., **11**, 5201 (2011).

Graphene-based organic photovoltaics

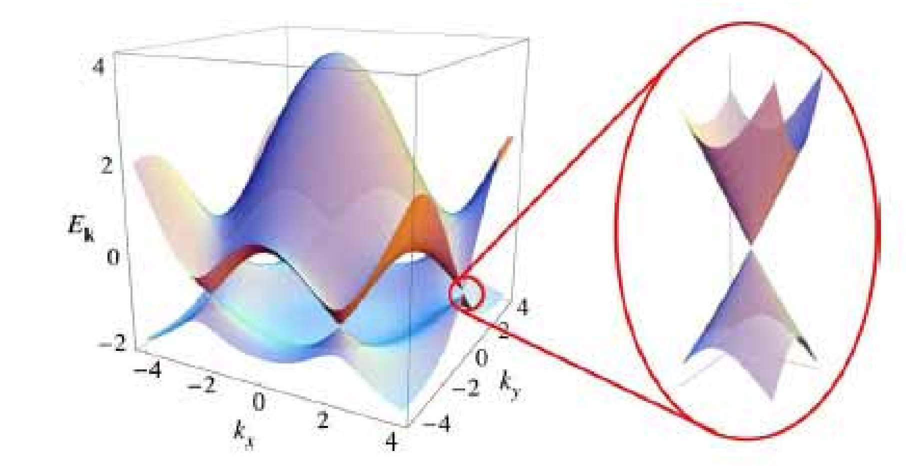


JPCL, **2**, 3006 (2011).

Today's Talk: Graphene Surface Chemistry



Novoselov et al., *PNAS* **102**, 10451 (2005)

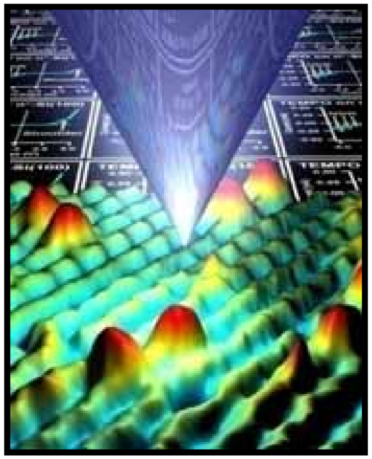


Neto et al., *Rev. Mod. Phys.* **81**, 109 (2009)

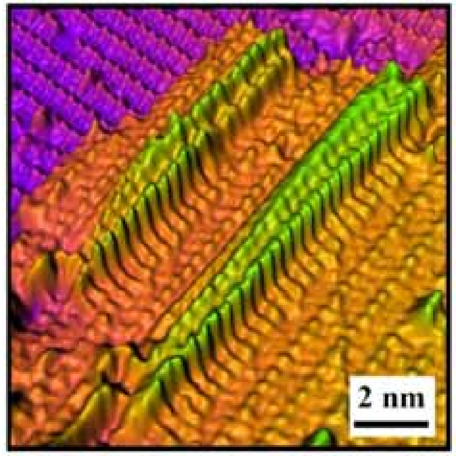
- The superlative and exotic electronic properties of graphene have been widely studied in condensed matter physics.
- However, to realize its full potential for electronic applications, interfaces with other materials will need to be precisely controlled.
- In addition to serving as a seeding layer for materials growth, chemical functionalization of graphene holds promise for tailoring electronic properties (e.g., doping, band gap control, etc.).

Past Work: Silicon Surface Chemistry

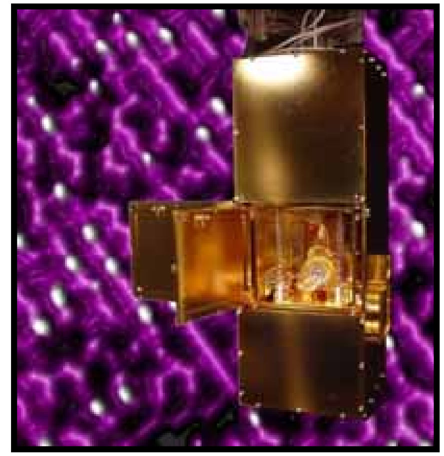
APL, **85**, 2619 (2004); *Nano Lett.*, **4**, 55 (2004); *PNAS*, **102,** 8838 (2005); *PRL*, **97**, 187601 (2006).



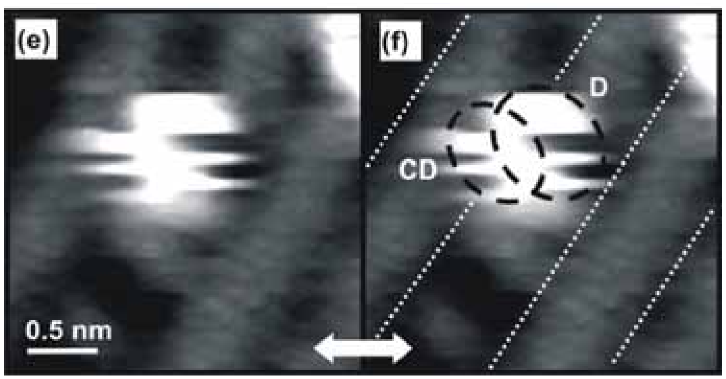
Single molecule characterization



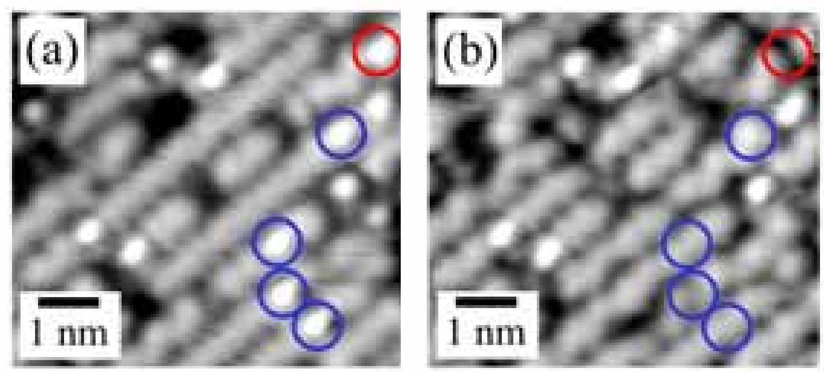
1-D heteromolecular nanostructures



Cryogenic STM spectroscopy



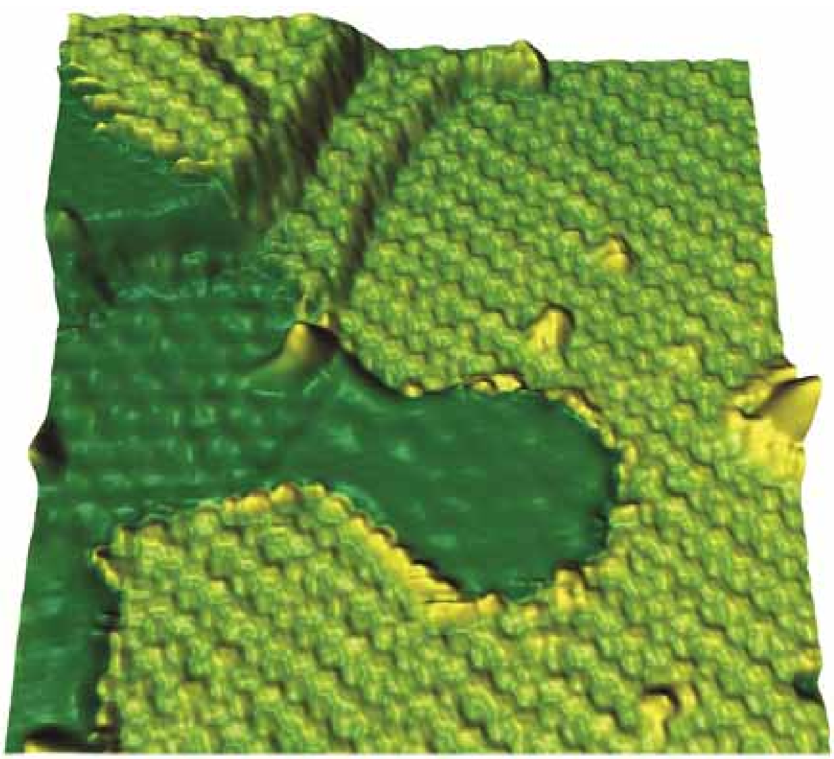
Current-driven molecular motion



Current-driven molecular desorption

Outline

Review Article:
MRS Bulletin, **36**, 532 (2011).



- Weakly interacting organic monolayers on graphene
  - PTCDA
  - Seeding layer for ALD
- Strongly interacting organic and inorganic adsorbates on graphene
  - PTCDI-C8
  - Organic free radicals
  - Atomic oxygen
- Nanopatterning on graphene
  - Nanoscale oxidation
  - Molecular heterostructures

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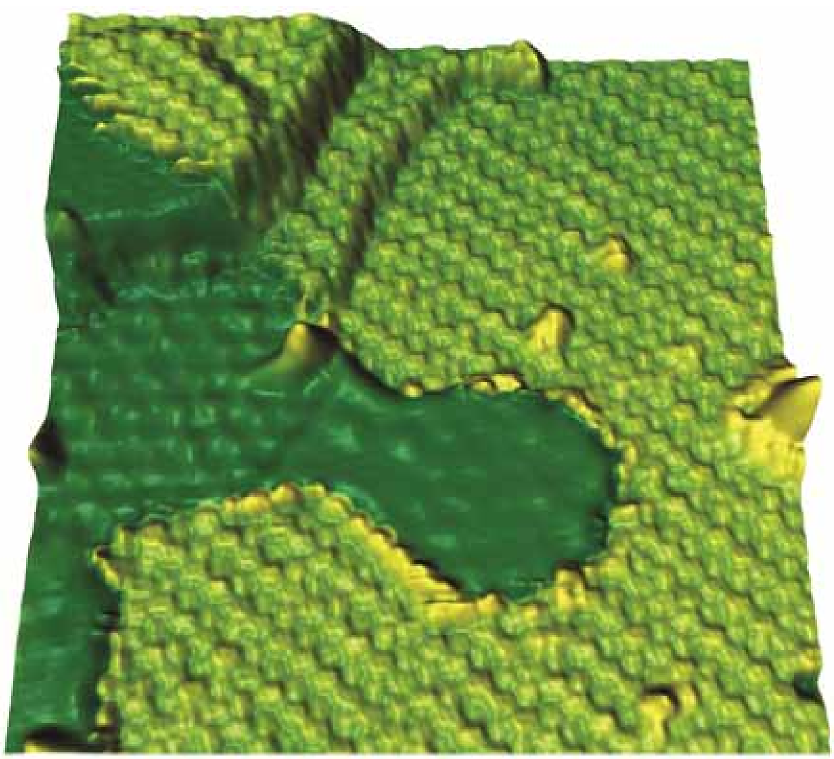
MRS Bulletin, **36**, 532 (2011).



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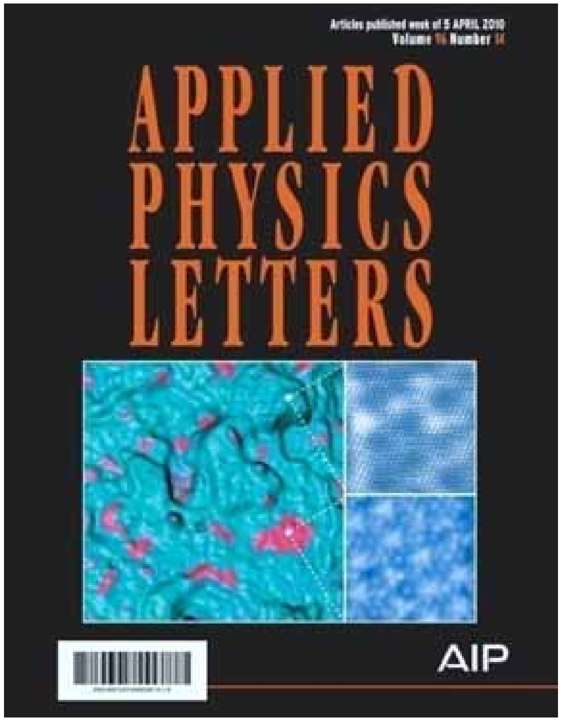
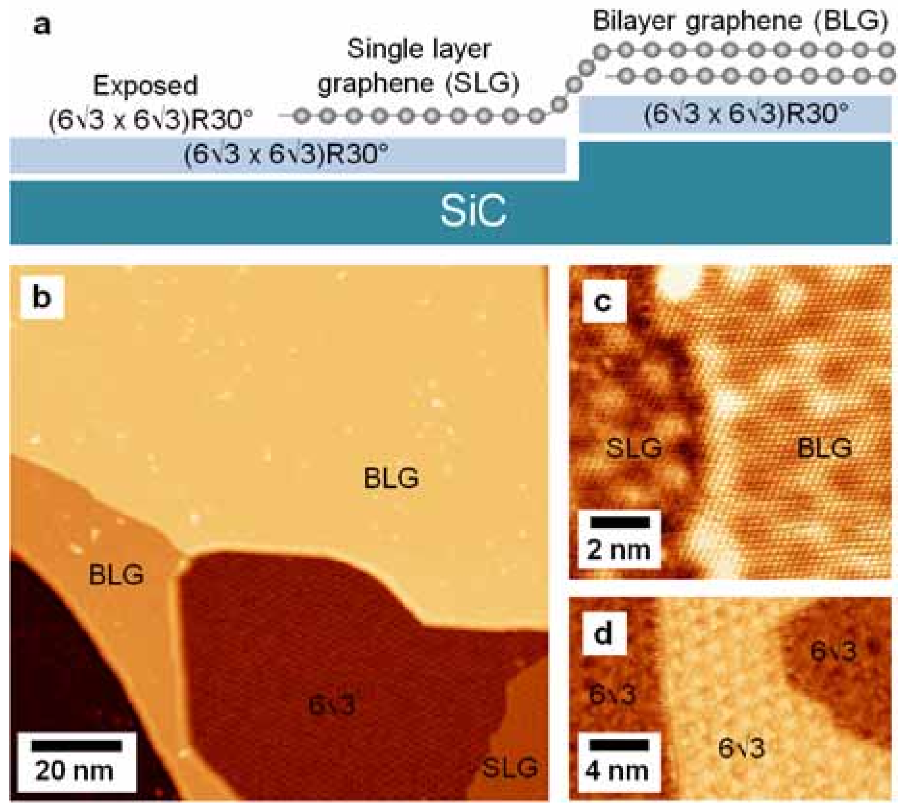
Preparation and UHV STM of Epitaxial Graphene

Applied Physics Letters, **96**, 143103 (2010).



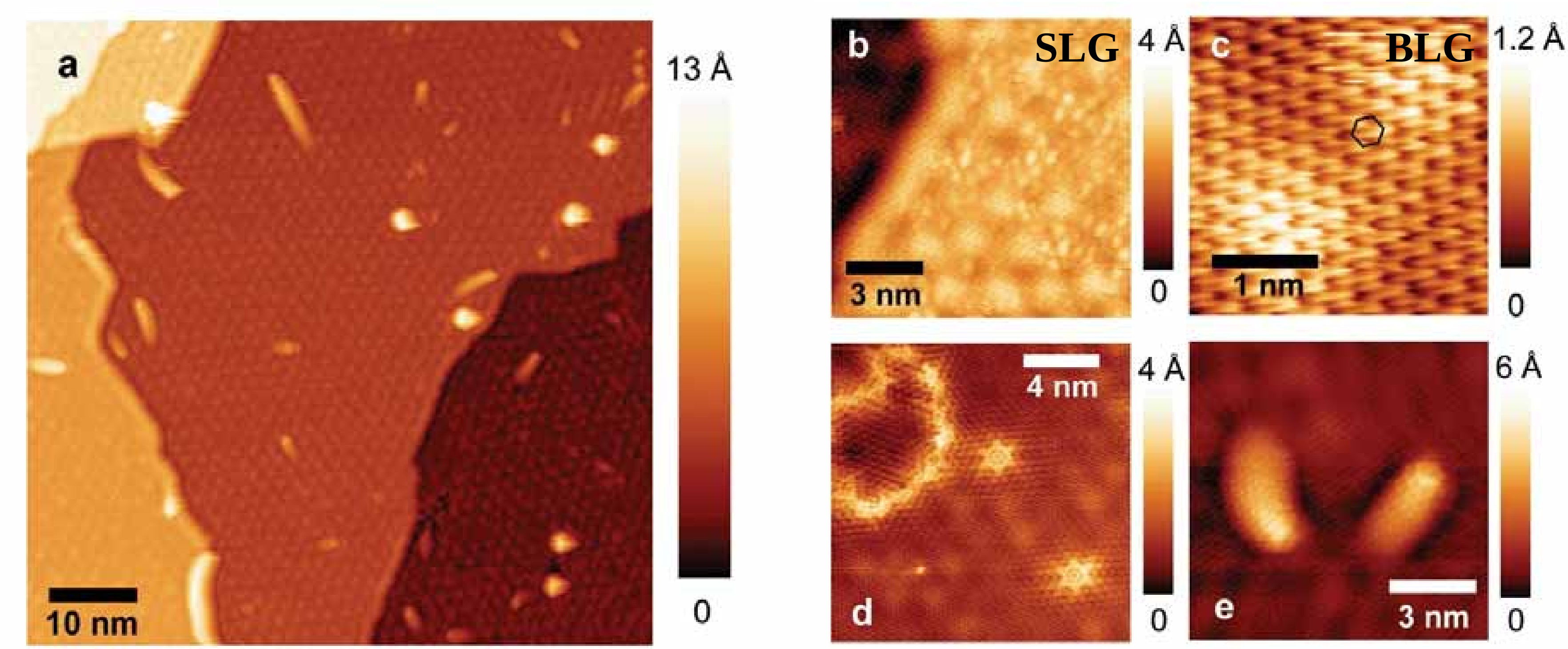
5 April 2010



- SiC(0001) graphitized by annealing in UHV at ~1350ºC
- Defect density and relative amount of SLG, BLG, and 6√3 depend on the details of the UHV processing

Surface Chemistry of Epitaxial Graphene

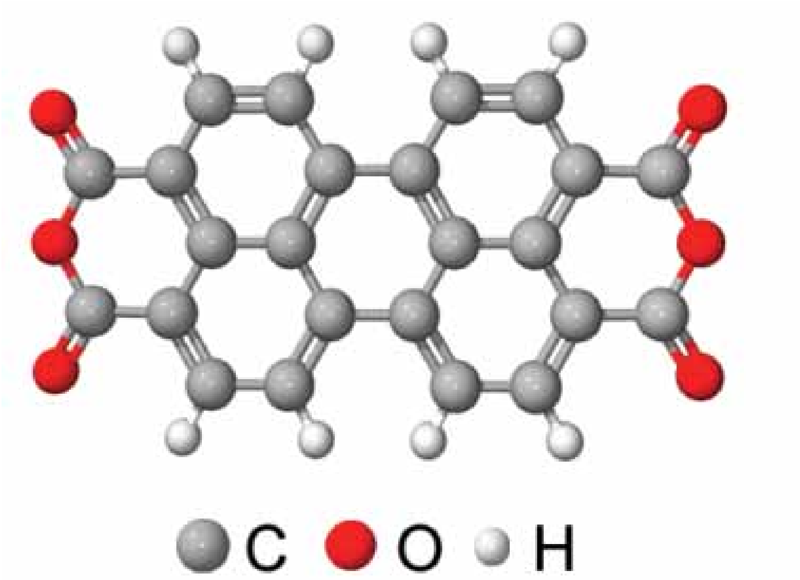
Review Article: *MRS Bulletin*, **36**, 532 (2011).

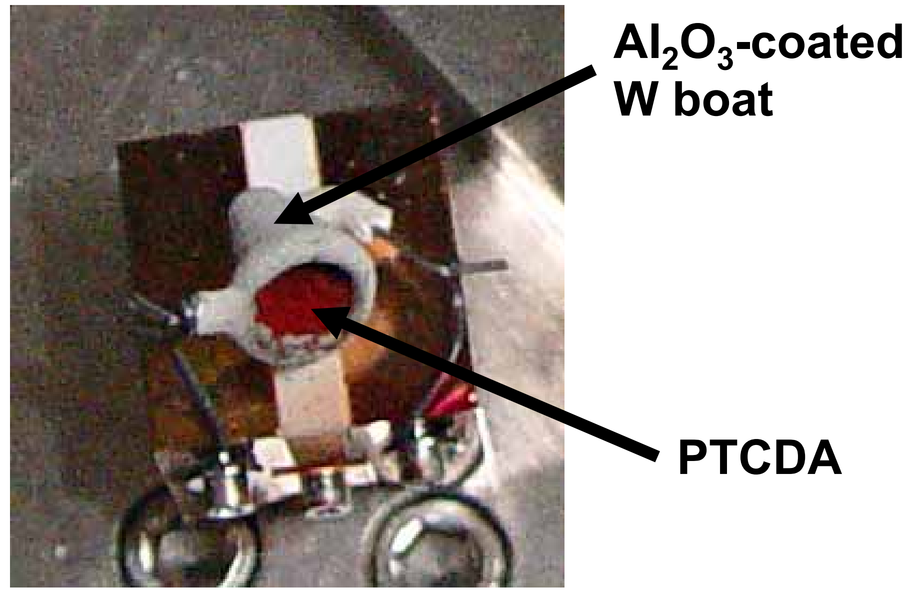


- Substrate: n-type SiC(0001)
- Graphitized by repeated annealing in UHV at ~1350ºC for 30 s
- Preparation conditions were chosen to yield a variety of surface defects to determine their influence on subsequent chemistry

PTCDA
(3,4,9,10-perylene-tetracarboxylic acid dianhydride)

Nature Chemistry, **1**, 206 (2009).

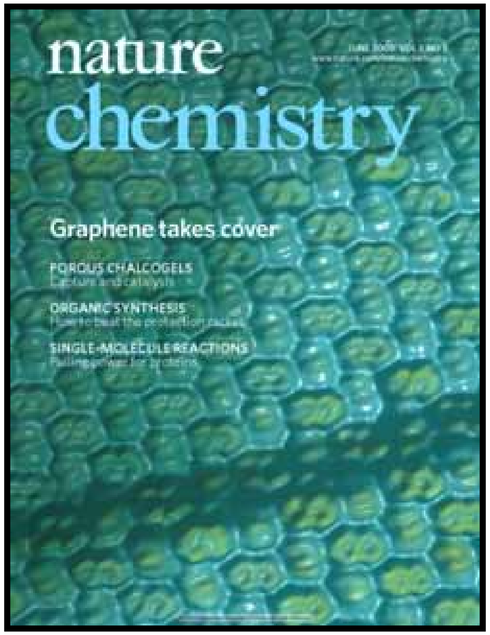


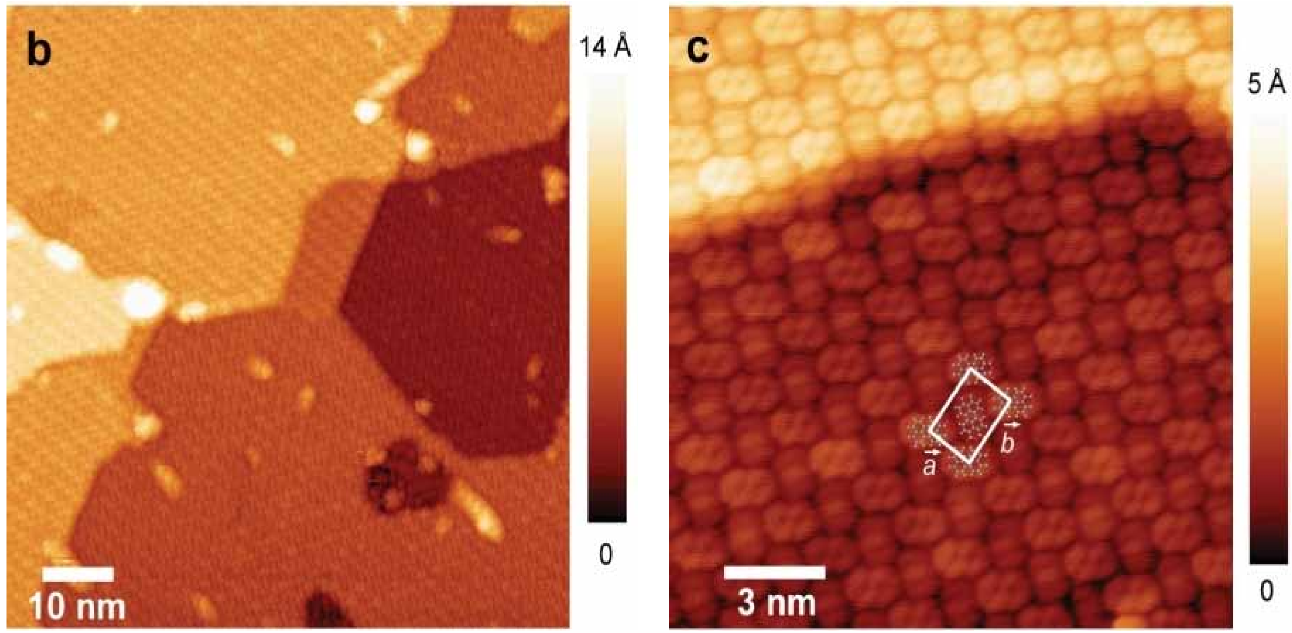


- Perylene-based molecule that forms ordered adlayers on graphite via noncovalent bonding (preserves sp^2 hybridization of graphene)
- Thermally stable → amenable to gas phase processing
- Crystalline molecular semiconductor that has been widely studied for organic thin film device applications

PTCDA Monolayer on Epitaxial Graphene

Nature Chemistry, **1**, 206 (2009).



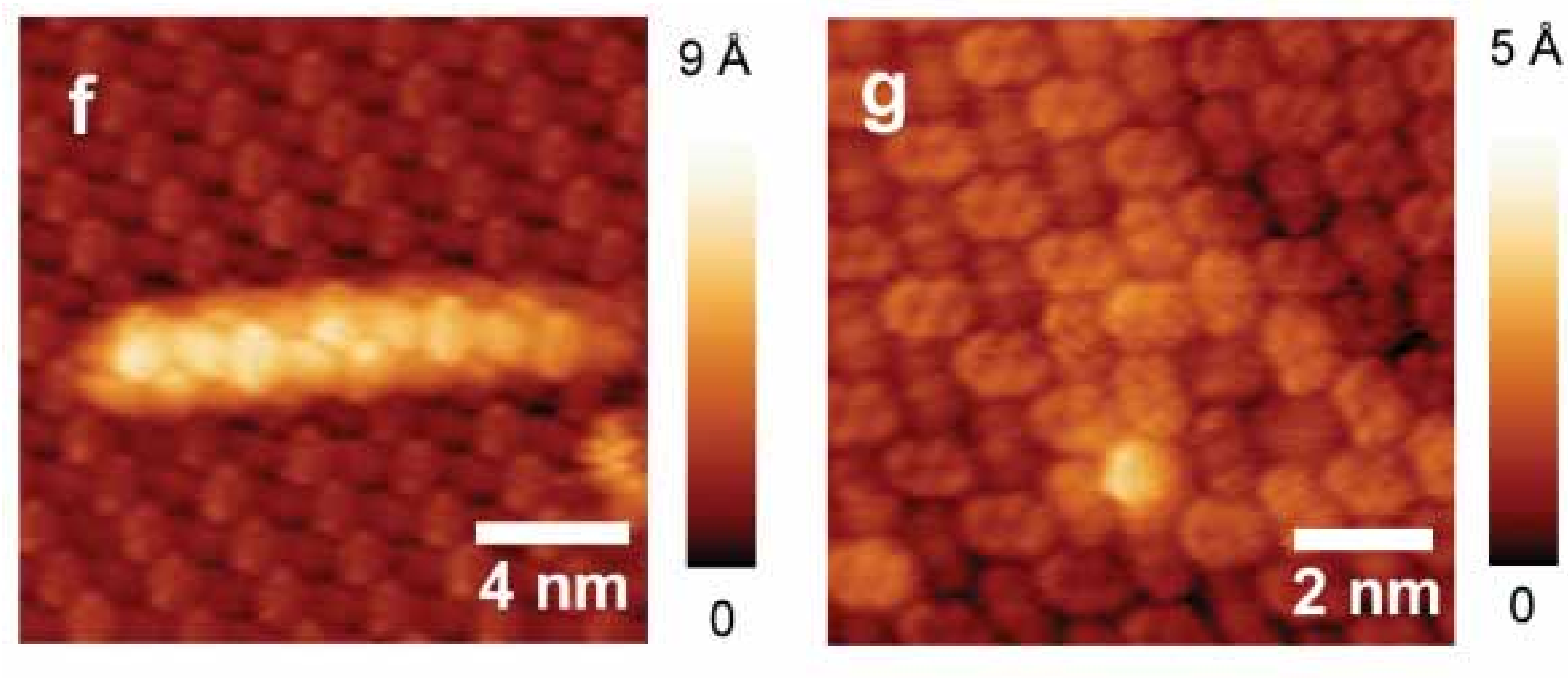


June, 2009

- Gas phase deposition of a monolayer of PTCDA
- Stable herringbone phase achieved at room temperature
- Long range order is observed including seamless continuity in molecular ordering over step edges

Insensitivity to Defects

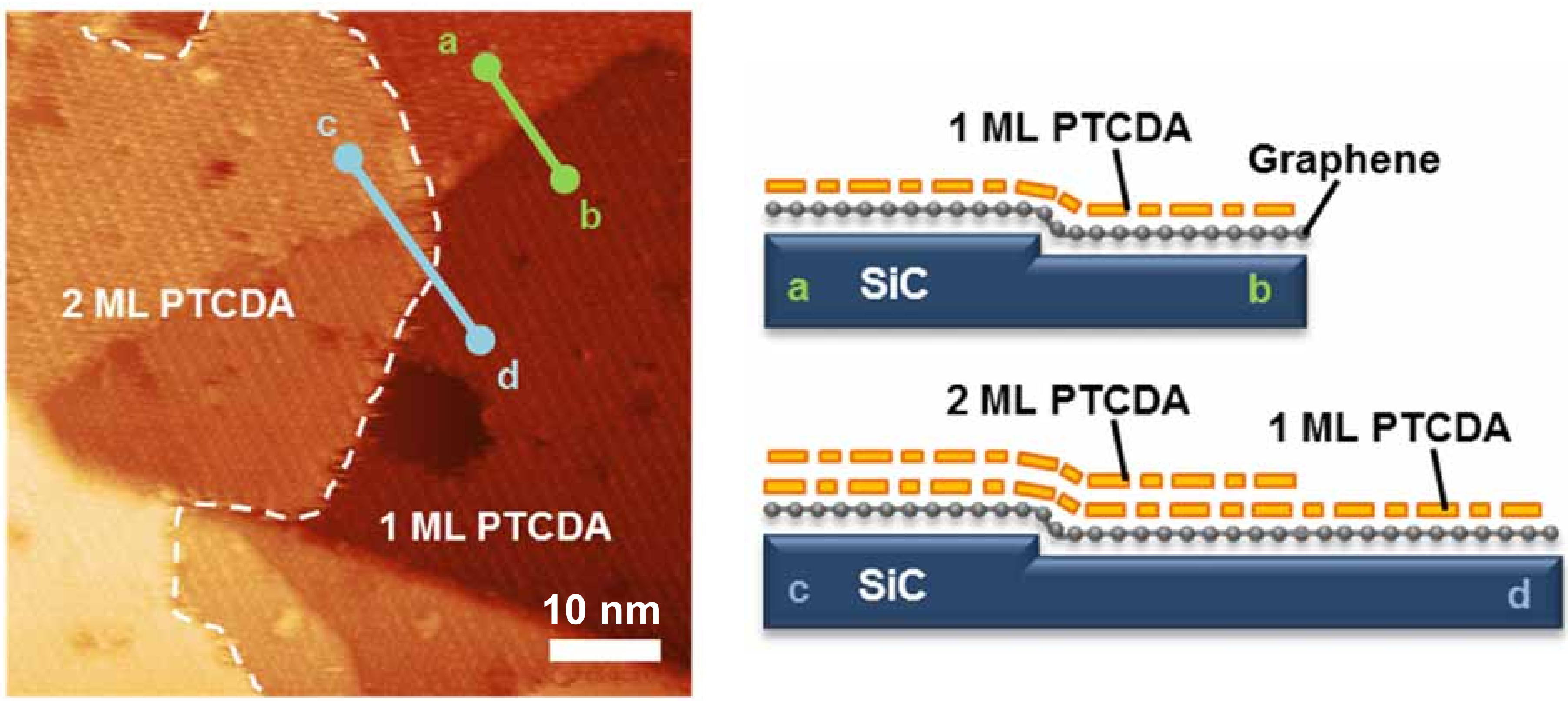
Nature Chemistry, **1**, 206 (2009).



- Ordering of the PTCDA monolayer is unperturbed by one-dimensional and point defects in the substrate
- Suggests that intermolecular interactions are more important than molecule-substrate interactions

PTCDA Growth Beyond One Monolayer

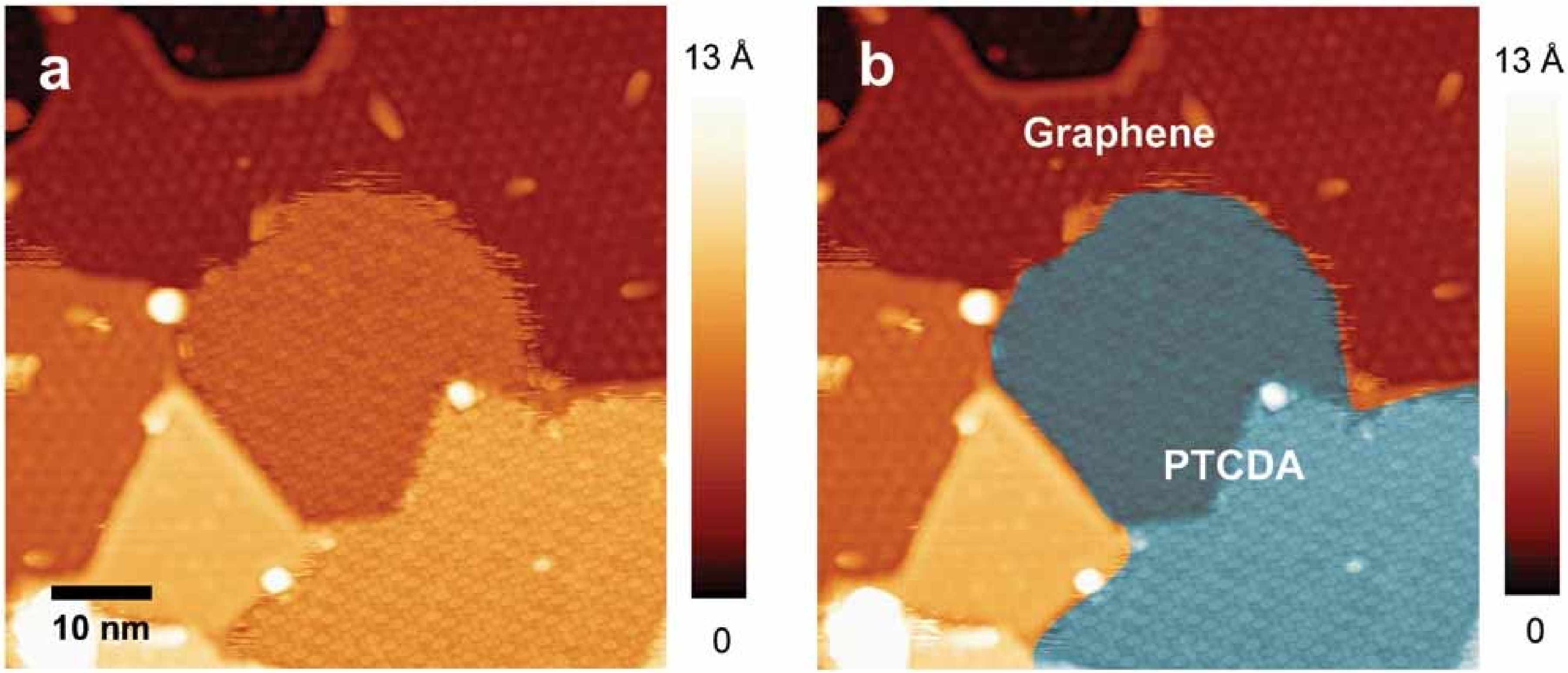
Surface Science, **605**, 1685 (2011).



- Layer-by-layer growth for the first 2 monolayers
- Thicker films transition to Stranski-Krastanov growth

Submonolayer Coverage

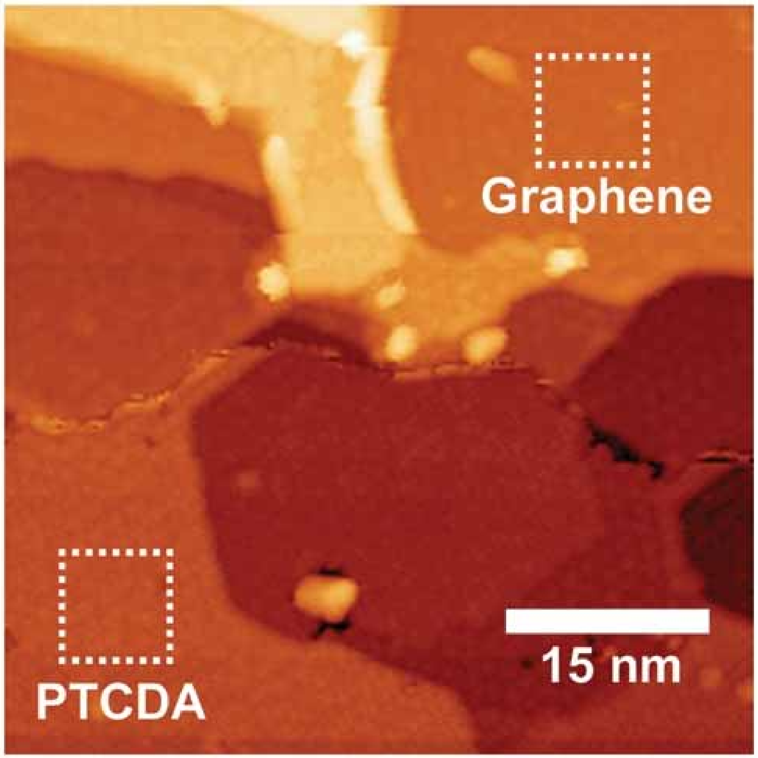
Nature Chemistry, **1**, 206 (2009).

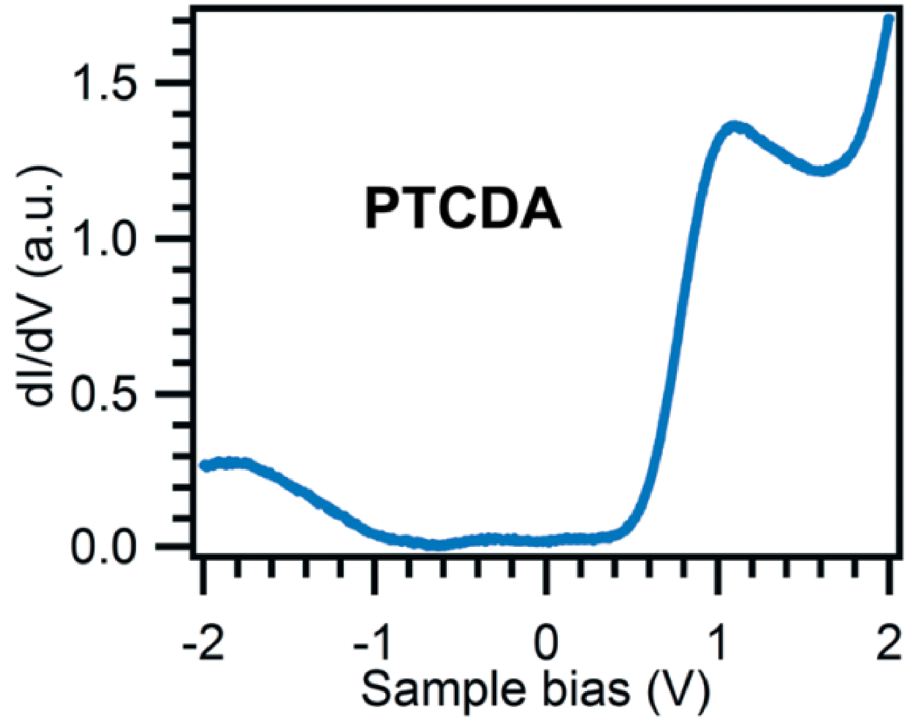


- Stable islands of PTCDA are observed at submonolayer coverage at room temperature
- Enables direct comparison between PTCDA and clean graphene

Tunneling Spectroscopy on PTCDA/Graphene

Nature Chemistry, **1**, 206 (2009).



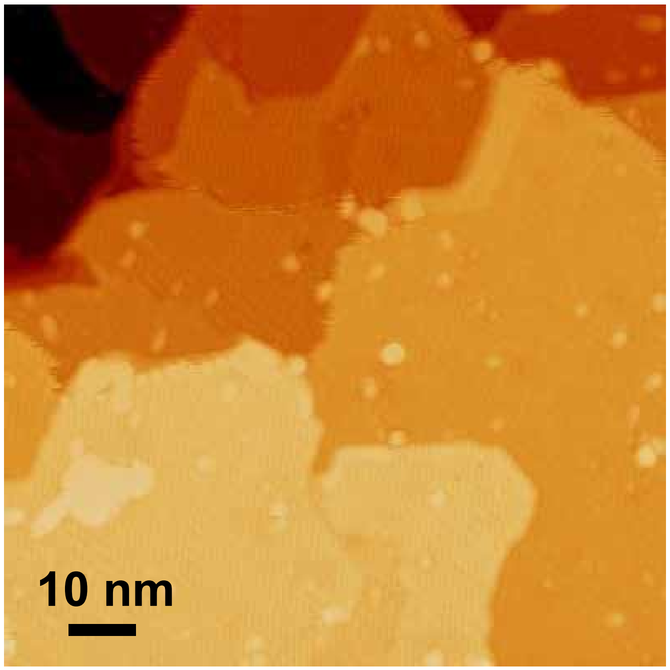


Tunneling spectra reconfirm weak interaction between PTCDA and graphene (i.e., PTCDA imparts chemical functionality with minimal electronic perturbation)

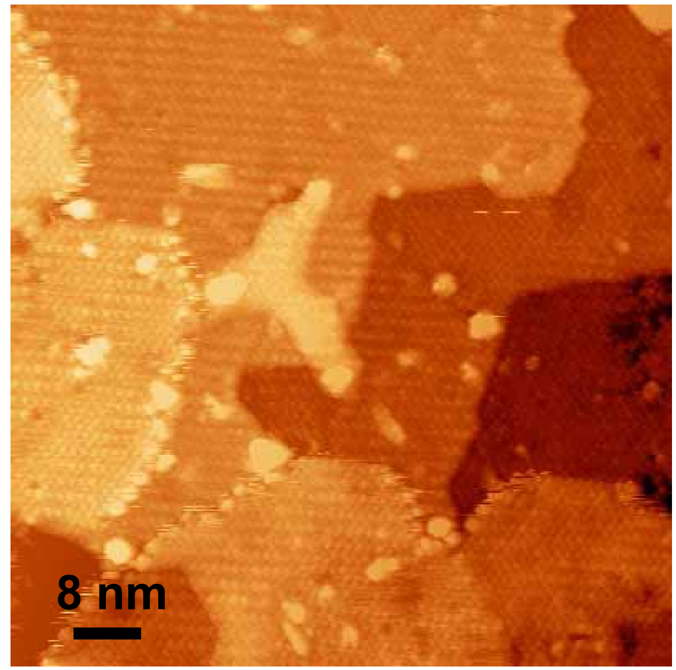
Chemical Robustness of the PTCDA Monolayer

Nature Chemistry, **1**, 206 (2009).

Before Ambient Exposure



After Ambient Exposure

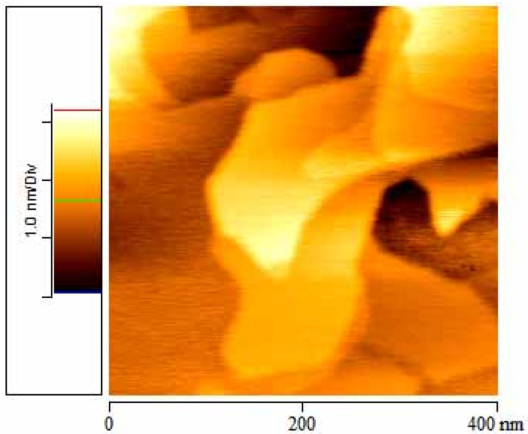


- Monolayer is brought out into ambient laboratory air for several minutes; then reintroduced to UHV and degassed
- Monolayer remains intact and pristine at the molecular scale, suggesting its use as a template for subsequent chemistry

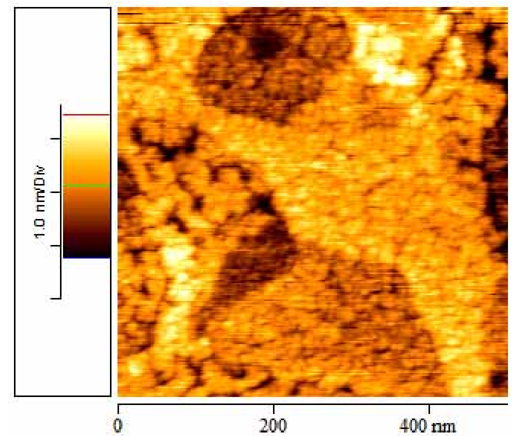
Seeding Atomic Layer Deposition on Graphene

ACS Nano, **5**, 5223 (2011).

Pristine Graphene:

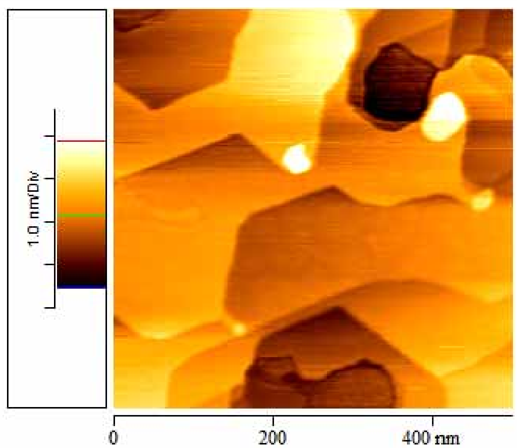


2 nm ALD Al_2O_3

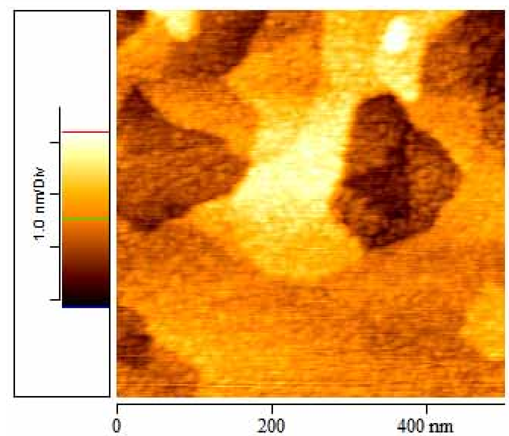


Discontinuous film riddled with pinholes

PTCDA-Graphene:



2 nm ALD Al_2O_3

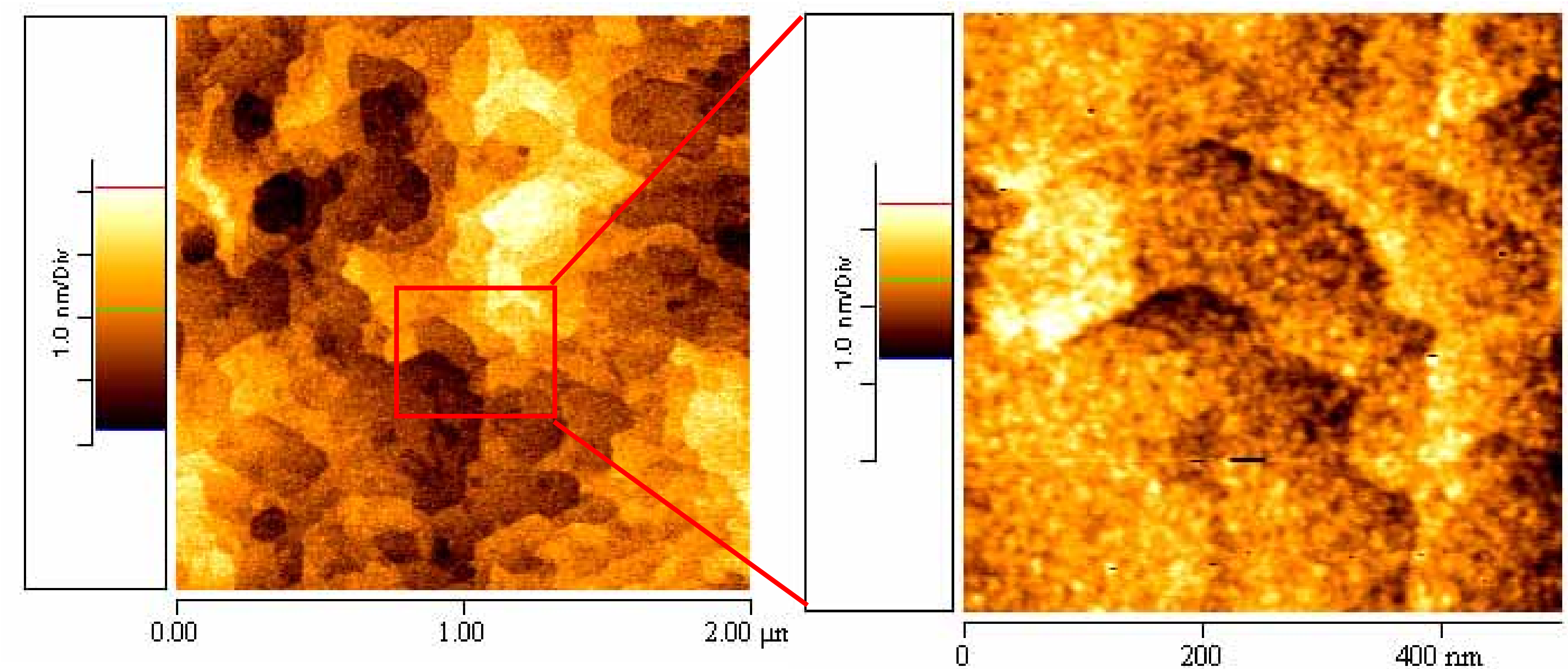


Continuous/ conformal film without pinholes

- Monolayer of PTCDA can seed ALD growth of dielectrics on graphene
- Other gas phase and liquid phase chemistries are under development

10nm Al_2O_3 on PTCDA-Graphene

ACS Nano, **5**, 5223 (2011).



• Even after 10 nm of Al_2O_3, ALD film uniformity is maintained across the surface of PTCDA functionalized graphene.
• Synchrotron X-ray reflectivity reveals no measurable change in the underlying graphene following PTCDA-seeded ALD.

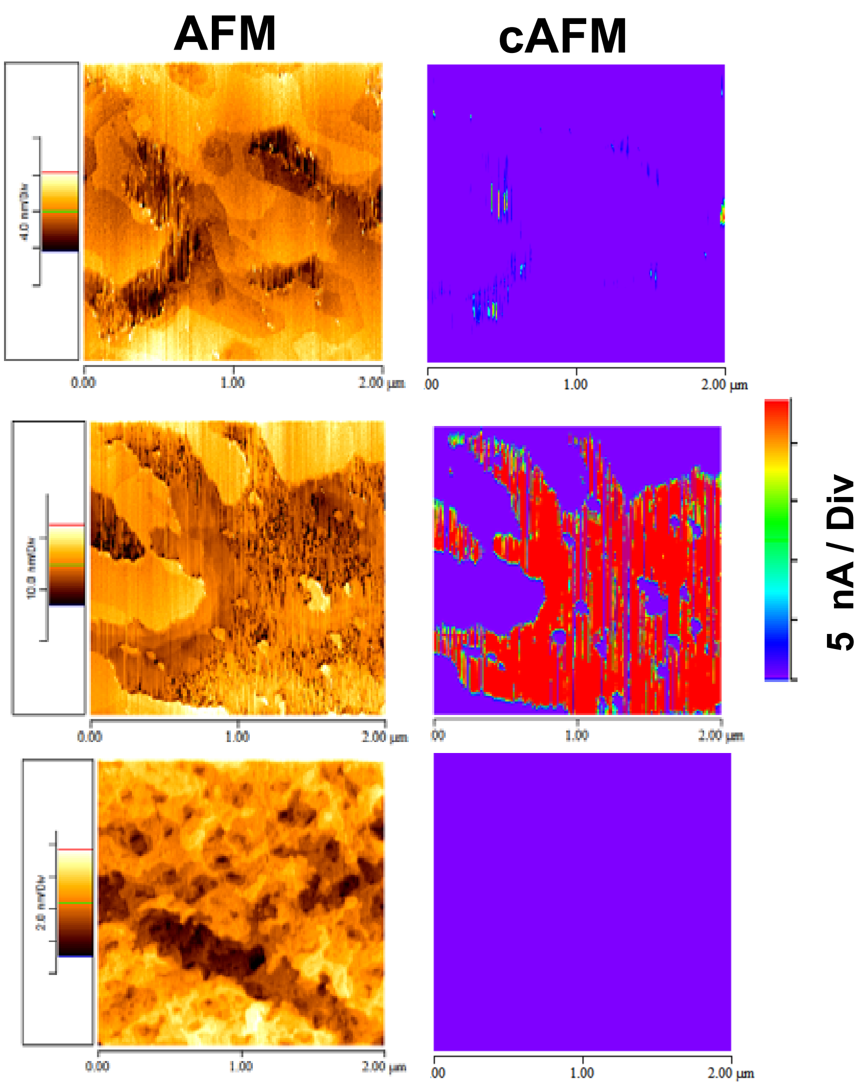
Superior Adhesion Provided by PTCDA

ACS Nano, **5**, 5223 (2011).

Al_2O_3 on Pristine Graphene 1st Scan

Al_2O_3 on Pristine Graphene 2nd Scan

Al_2O_3 on PTCDA-Graphene

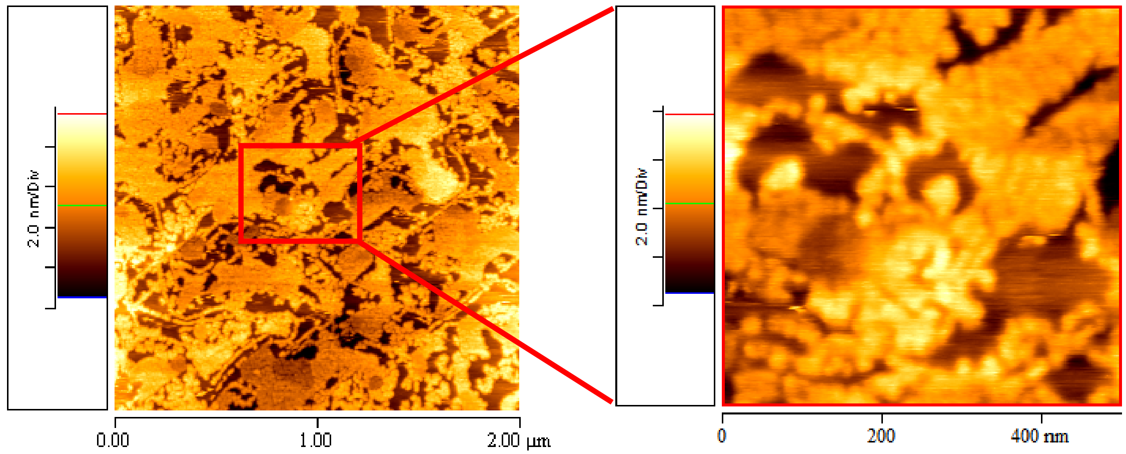


- Even under minimal contact forces (~10 nN), contact mode AFM scratches off Al_2O_3 (~2nm) from pristine graphene
- Al_2O_3 (~2nm) on PTCDA-Graphene is unperturbed by contact mode AFM
- Similar results have been achieved for HfO_2

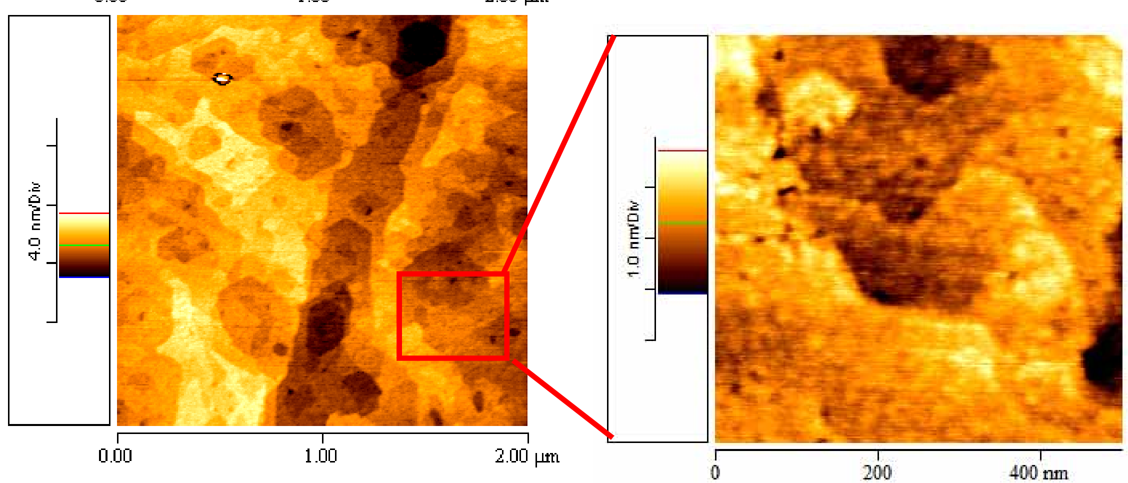
Atomic Layer Deposition of HfO_2

ACS Nano, **5**, 5223 (2011).

Pristine Graphene: After ~2.5 nm of HfO_2



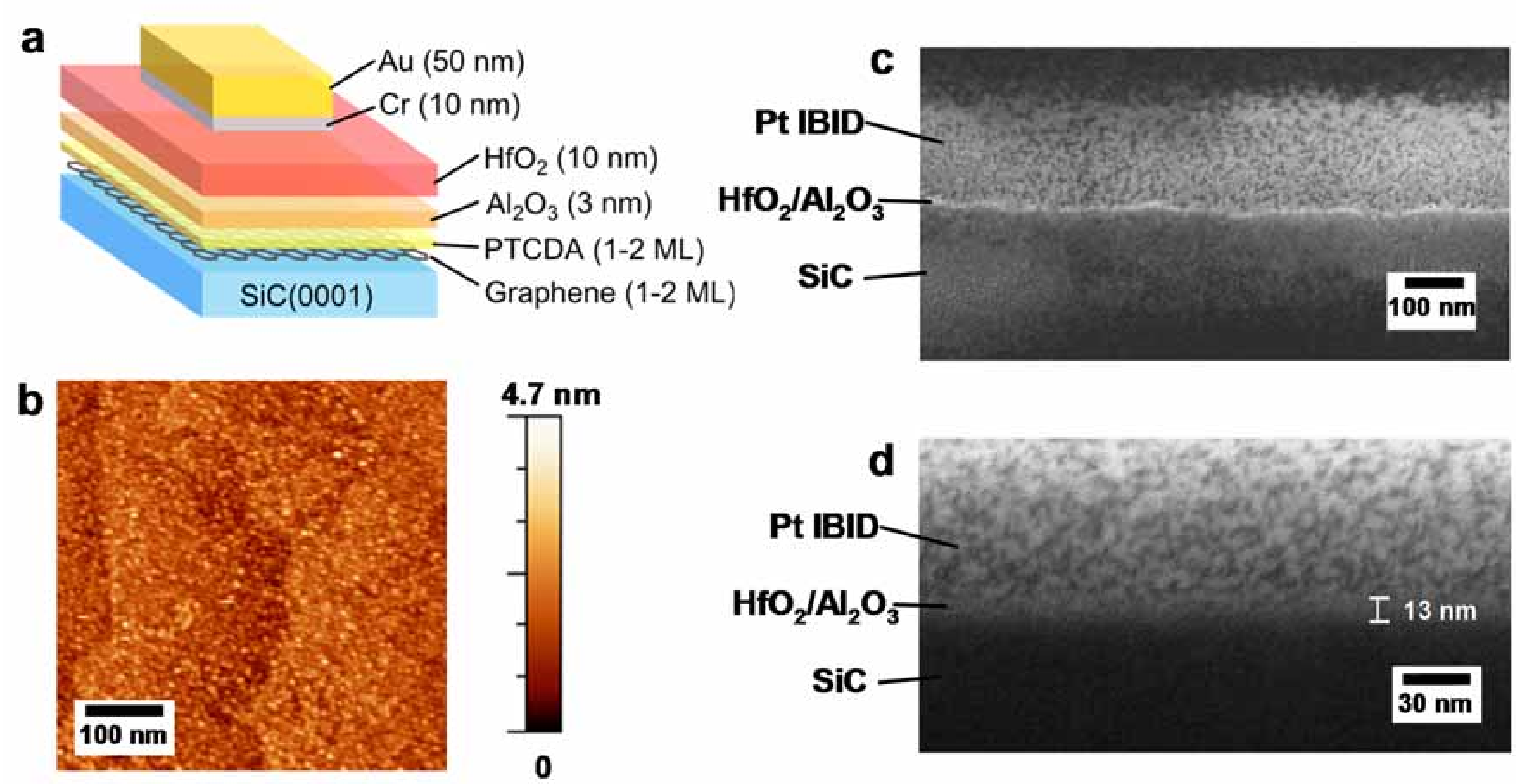
PTCDA-Graphene: After ~2.5nm of HfO_2



- Improved conformality for ALD hafnia on PTCDA/graphene

Metal/Oxide/Graphene Capacitor Structures

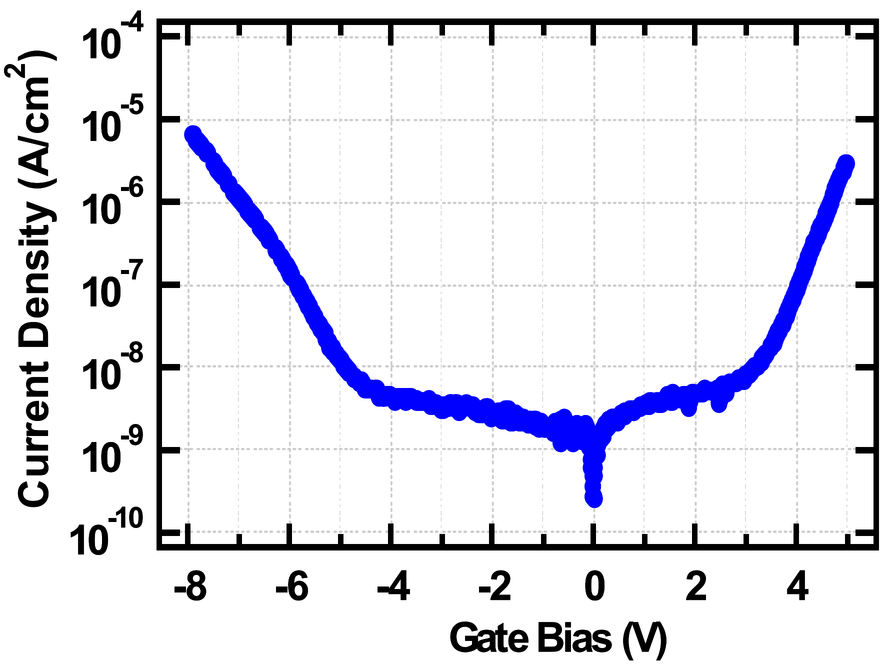
ACS Nano, **5**, 5223 (2011).

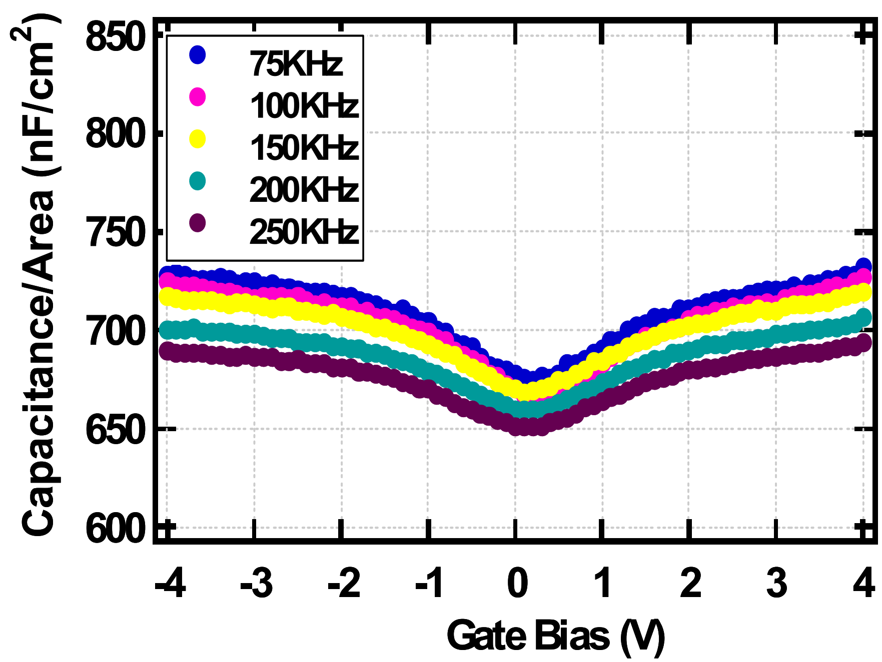


- Dielectric structure: PTCDA + 3 nm ALD Al_2O_3 + 10 nm ALD HfO_2
- AFM and SEM confirm highly conformal growth of dielectric stack

Metal/Oxide/Graphene Electrical Measurements

ACS Nano, **5**, 5223 (2011).

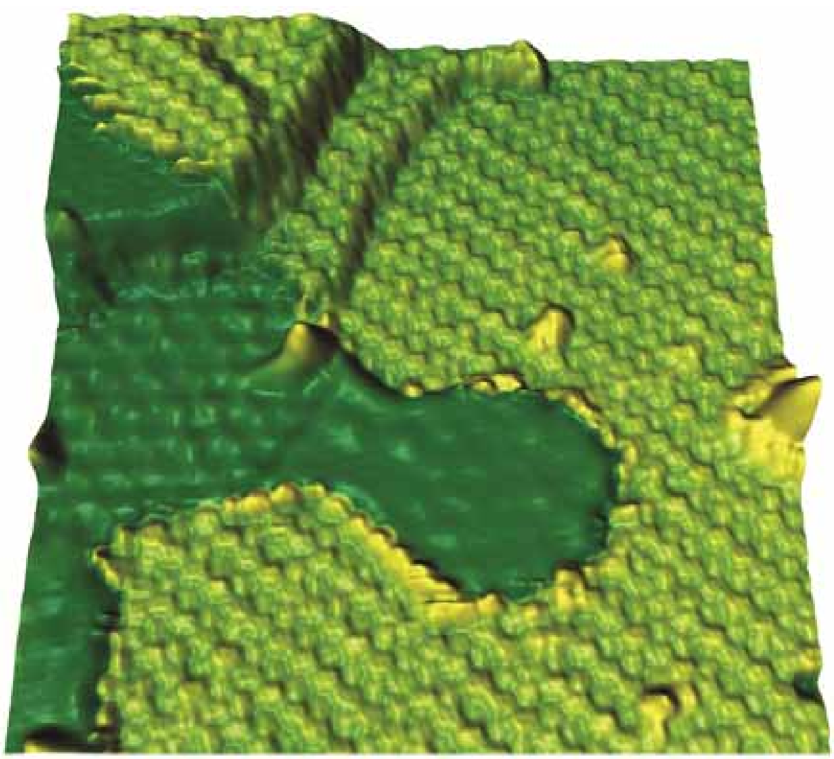




- Low pinhole density and leakage current for 100 μm test structures
- Capacitance measurement implies $k_{alumina}$ = 5.6 and k_{hafnia} = 13
- Low hysteresis suggests low interface trap density

Outline

Review Article:
MRS Bulletin, **36**, 532 (2011).



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- Nanopatterning on graphene
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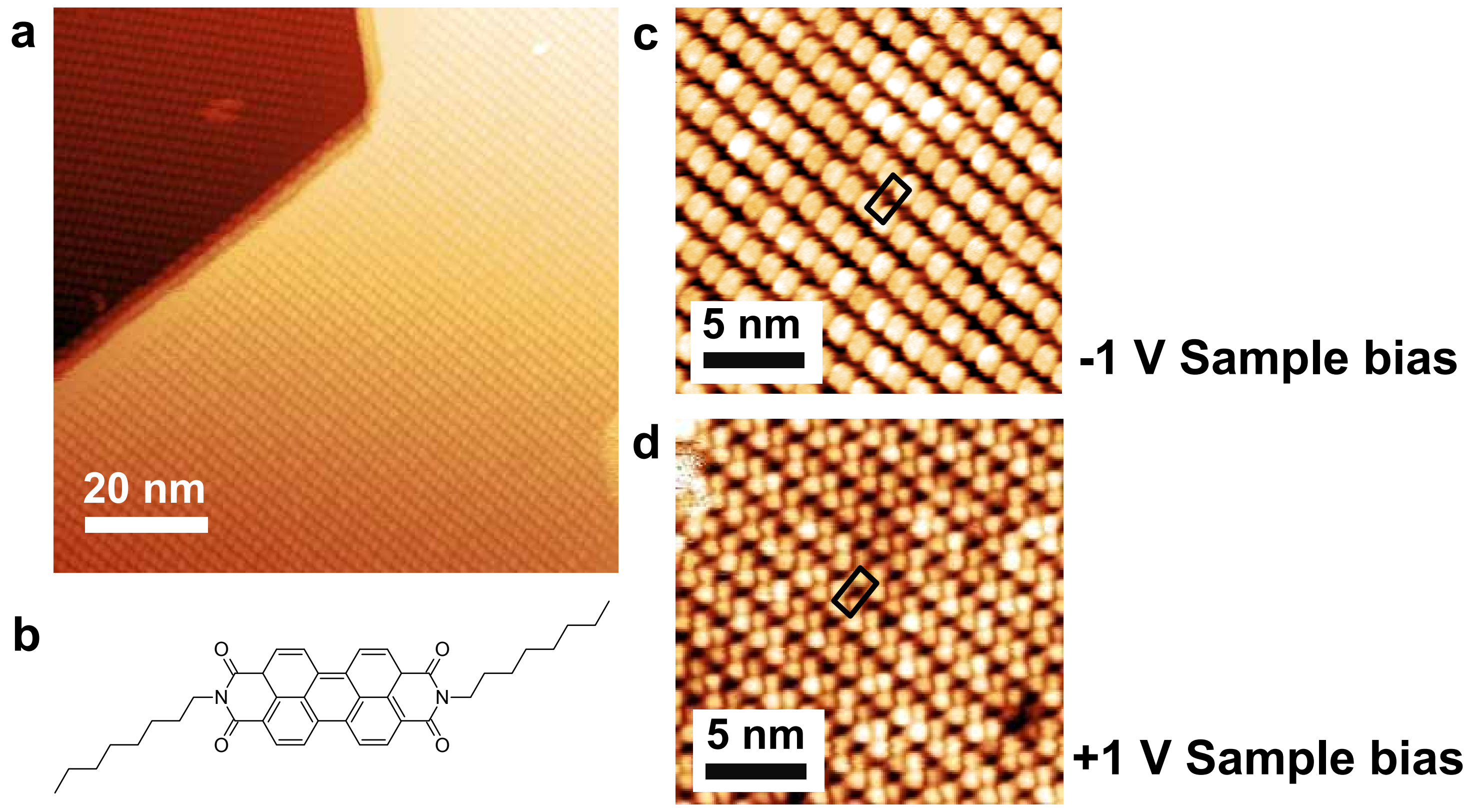
PTCDI-C8 Monolayers on Epitaxial Graphene

Nano Letters, **11**, 589 (2011).

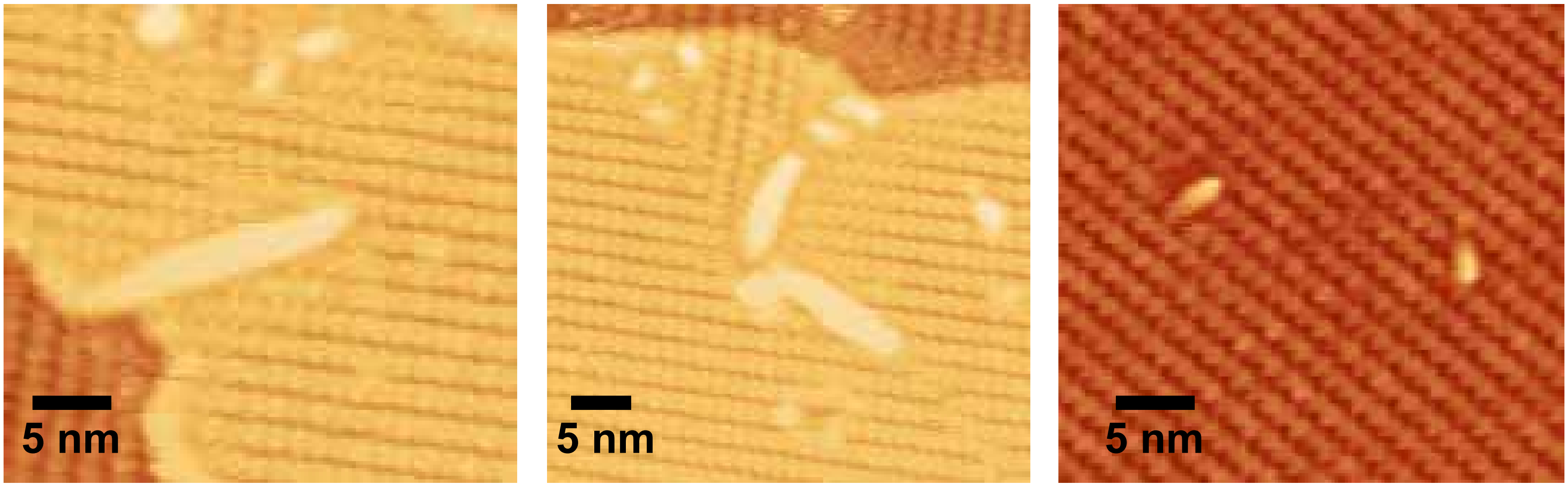
N,N′-dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8)



- Self-assembled monolayers of PTCDI-C8 on epitaxial graphene show different ordering than PTCDA

Defect Interactions with PTCDI-C8

Nano Letters, **11**, 589 (2011).

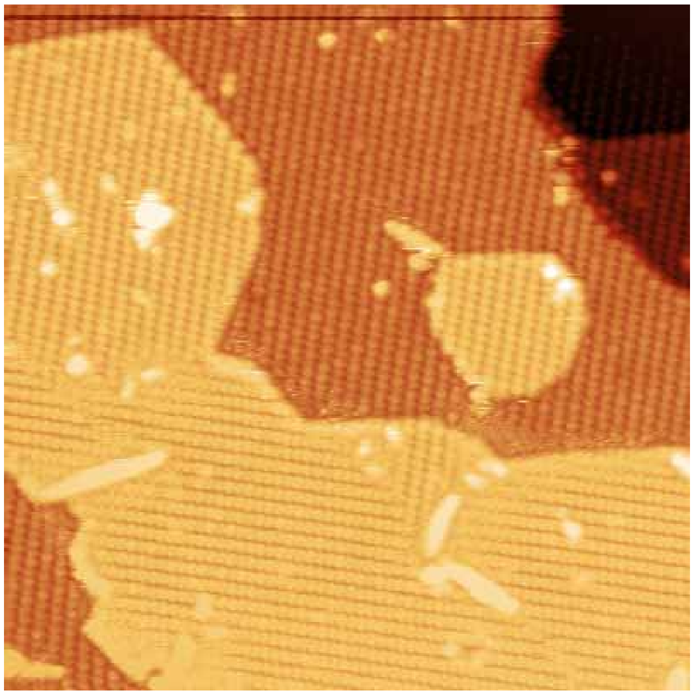


- Unlike PTCDA, PTCDI-C8 ordering is interrupted by defects
- Smaller defects are surrounded by PTCDI-C8; larger defects can affect formation of new domains
- Intermolecular forces in PTCDI-C8 monolayer likely weaker than in PTCDA monolayer

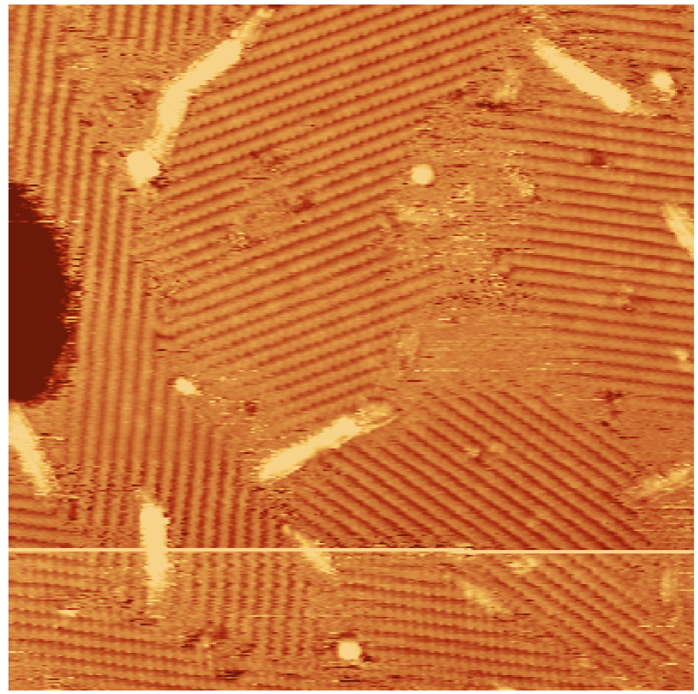
Chemical Robustness of the PTCDI-C8 Monolayer

Nano Letters, **11**, 589 (2011).

Before ambient exposure



After 12 hr ambient exposure

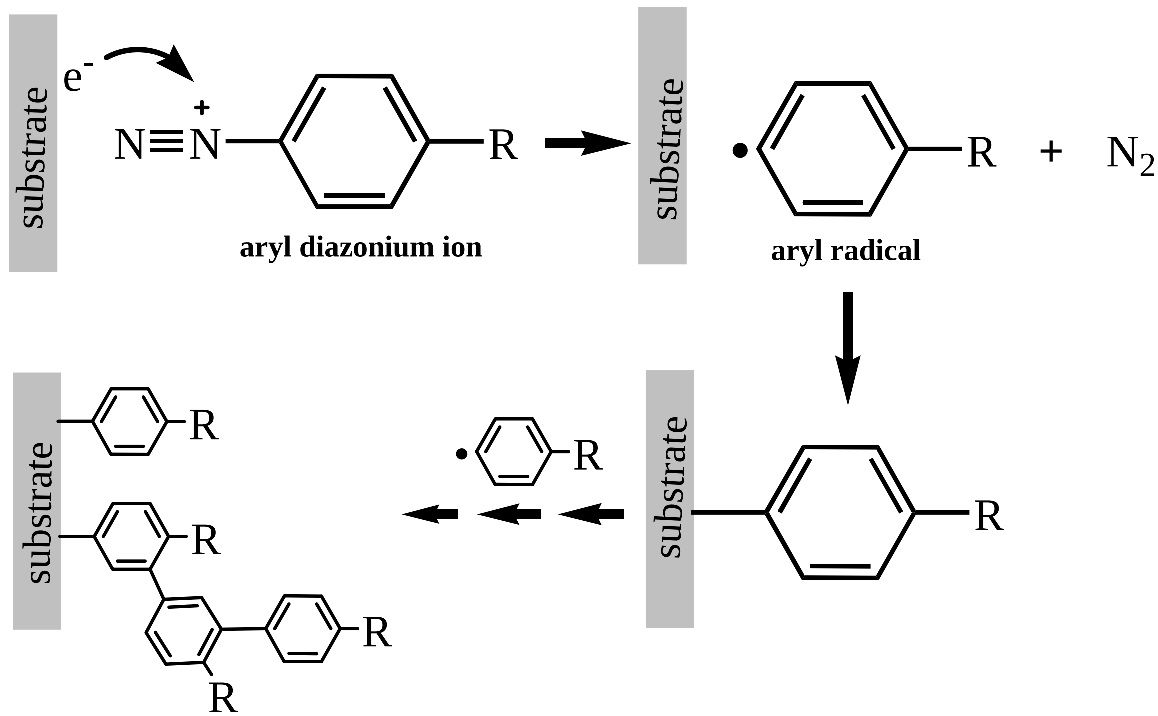


- PTCDI-C8 monolayer was brought out into ambient laboratory air for 12 hours, then reintroduced to UHV and degassed
- Monolayer ordering and cleanliness are maintained

Covalent Chemistry on Epitaxial Graphene

JACS **1992**, *114*, 5883; *Chem. Mater.* **2006,** *18,* 2021; *JACS* **2009**, *131*, 1336.

Reaction scheme for aryldiazonium salt:

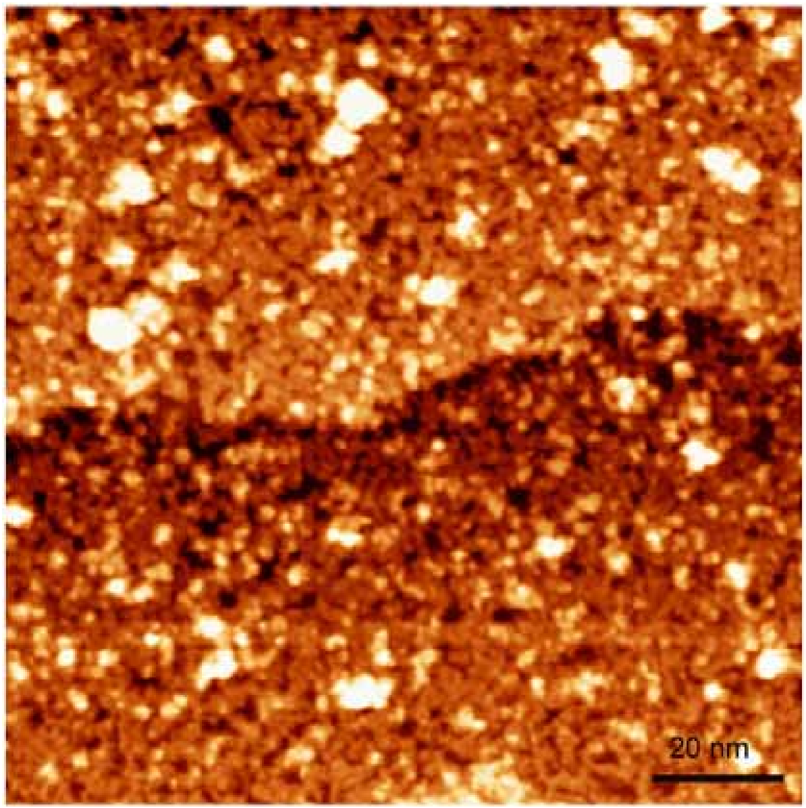


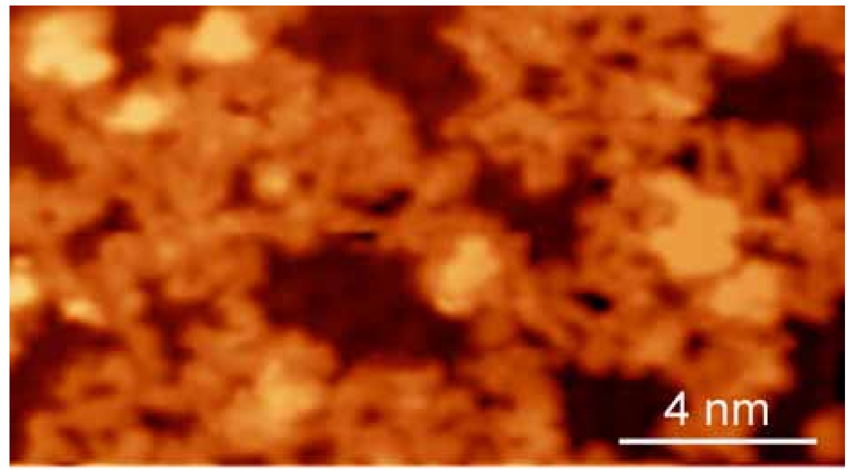
- Covalent functionalization of graphene recently demonstrated via reduction of aryldiazonium salt in solution
- Disruption of graphene sp^2 hybridization influences electronic properties
- Radical mediated chemistry may lead to polymerization

UHV STM of Covalently Arylated Graphene

Journal of the American Chemical Society, **132**, 15399 (2010).

SiC-graphene dipped into 4-nitrophenyldiazonium salt solution in glove box followed by degassing at 500ºC in UHV

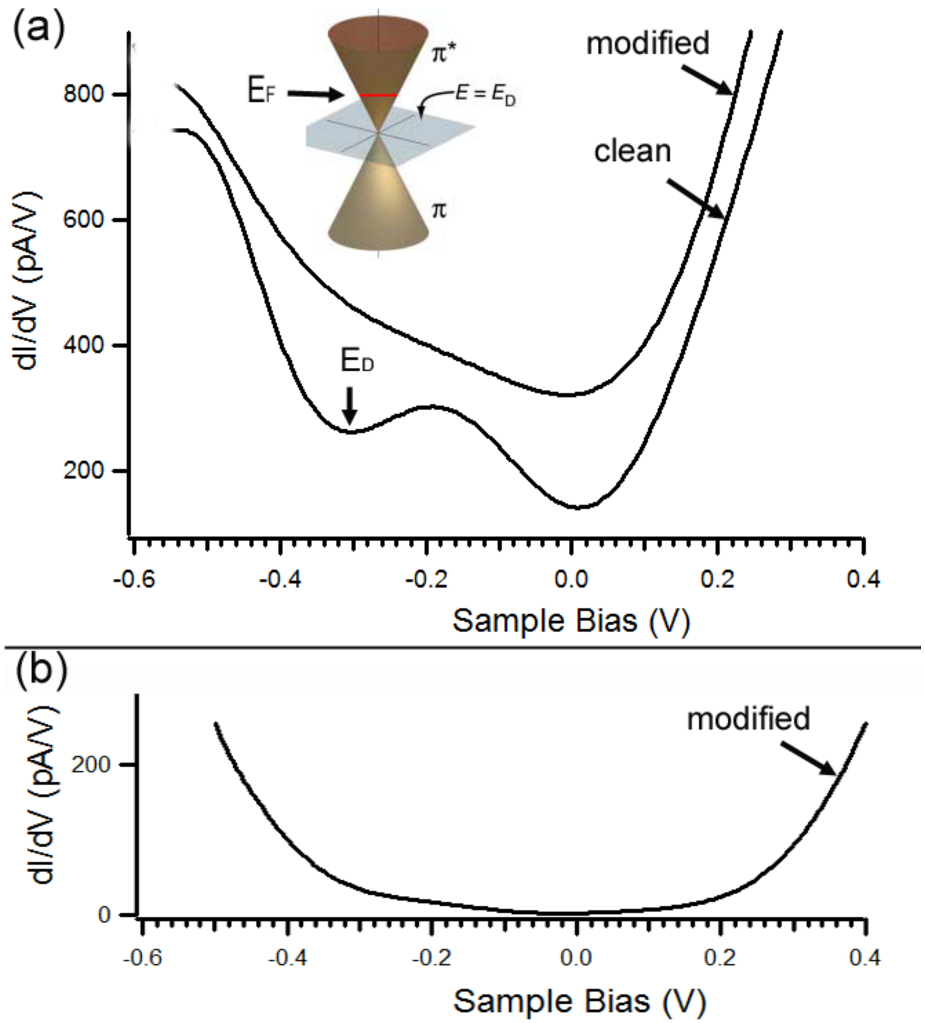




- Strong evidence for polymerization
- Robust in atmosphere
- Local perturbation to electronic properties at covalent binding sites

STS on Covalently Arylated Bilayer Graphene

Journal of the American Chemical Society, **132**, 15399 (2010).

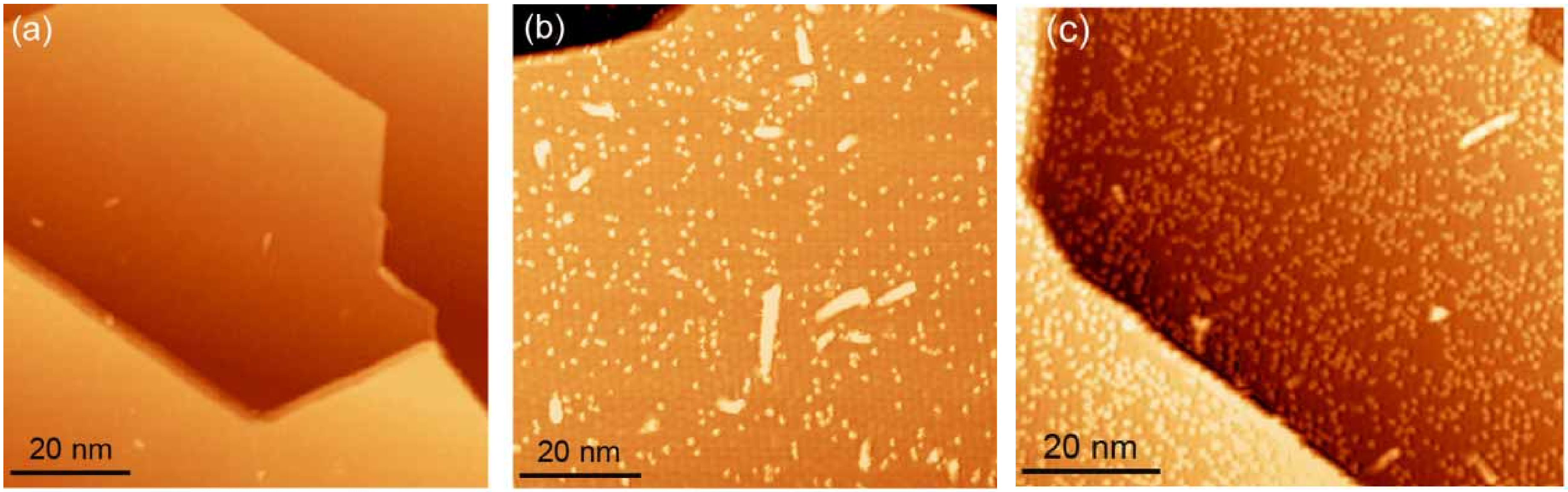


- Clean bilayer graphene shows a minimum in dI/dV at -0.3 V (i.e., n-type)
- On the arylated surface, the minimum at -0.3 V is not observed but finite dI/dV is still present at all biases
- In a small number of cases (~ 5%), a band gap is observed on the arylated surface (presumably at covalent binding sites)

Covalently Modifying Graphene with Atomic Oxygen

Nature Chemistry, **4**, 305 (2012).

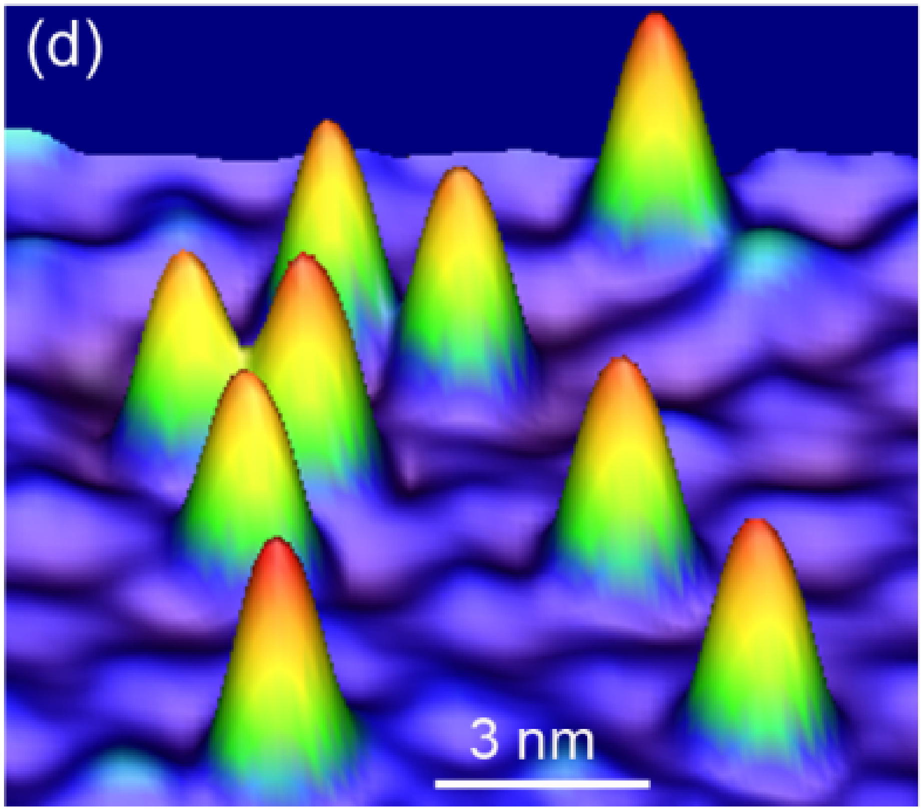
Pristine Graphene | **600 L of Atomic O** | **2400 L of Atomic O**

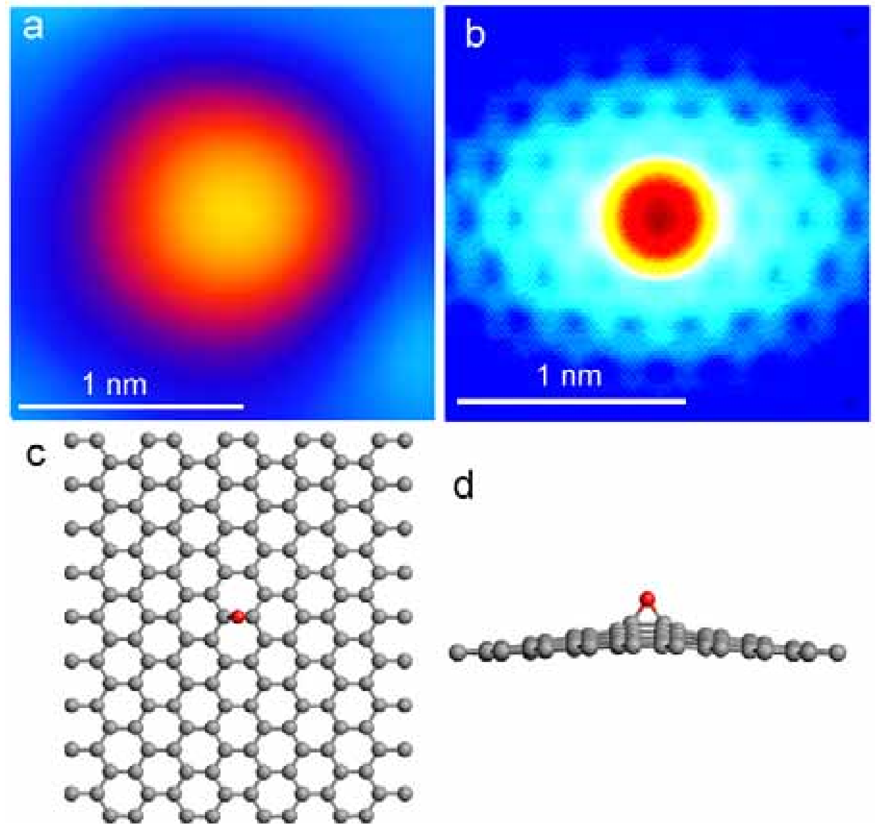


- Atomic oxygen is generated in UHV by cracking molecular oxygen on a hot (~1500ºC) tungsten filament.
- Bright protrusions are attributed to chemisorbed oxygen species.

High Resolution STM and Density Functional Theory

Nature Chemistry, **4**, 305 (2012).

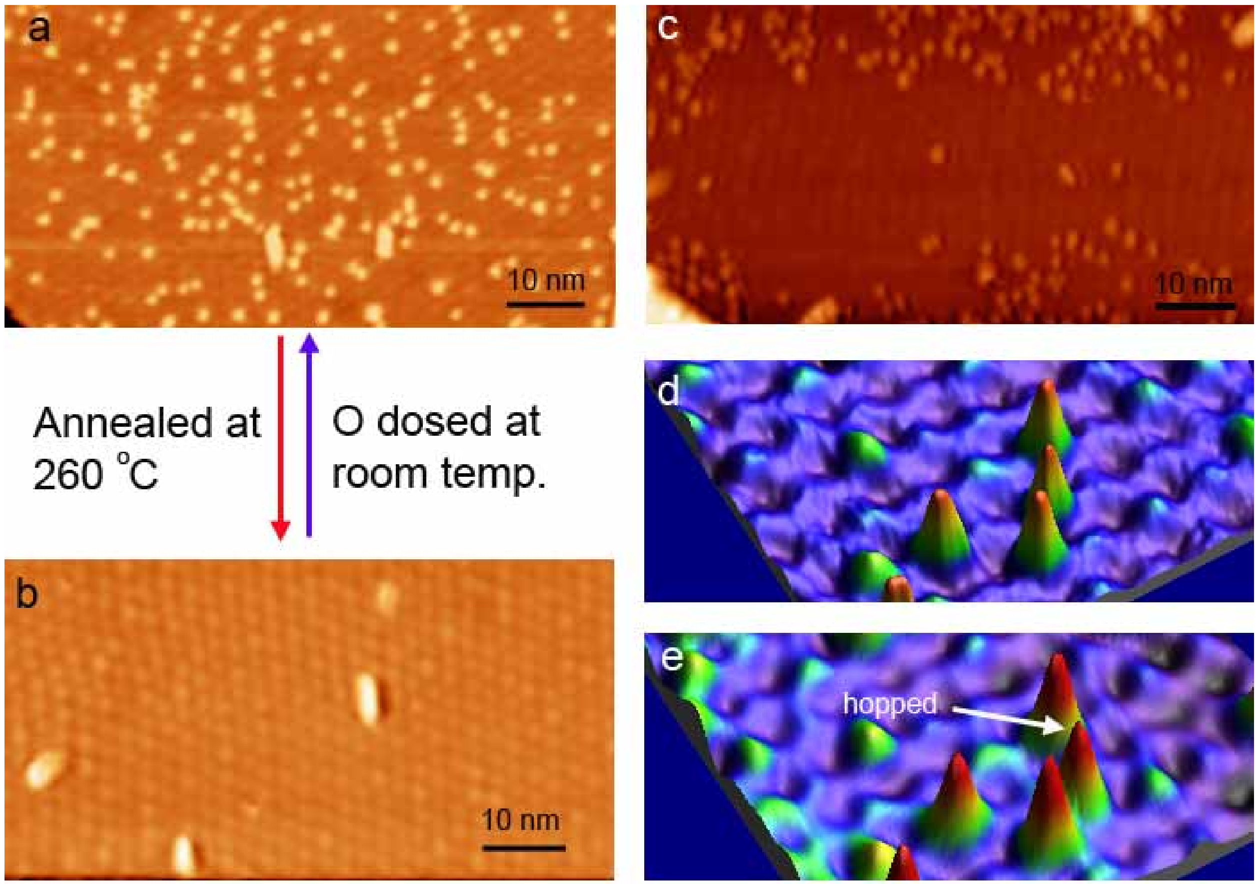




- Uniformity of features in STM implies one primary binding configuration.
- Comparison with DFT calculations suggests epoxy functionalization.

Reversible UHV Oxidation and Reduction

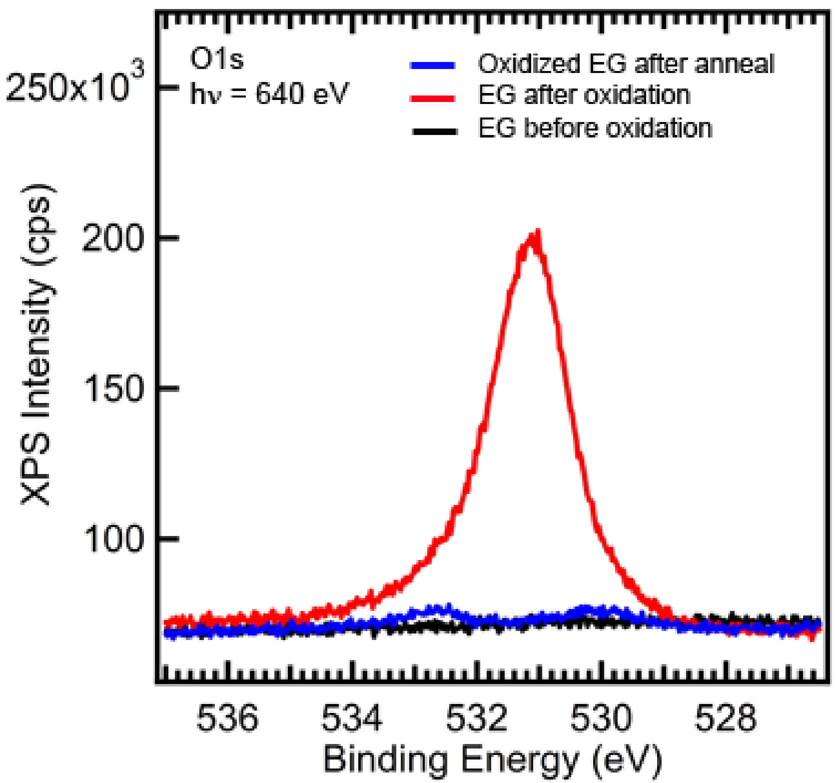
Nature Chemistry, **4**, 305 (2012).

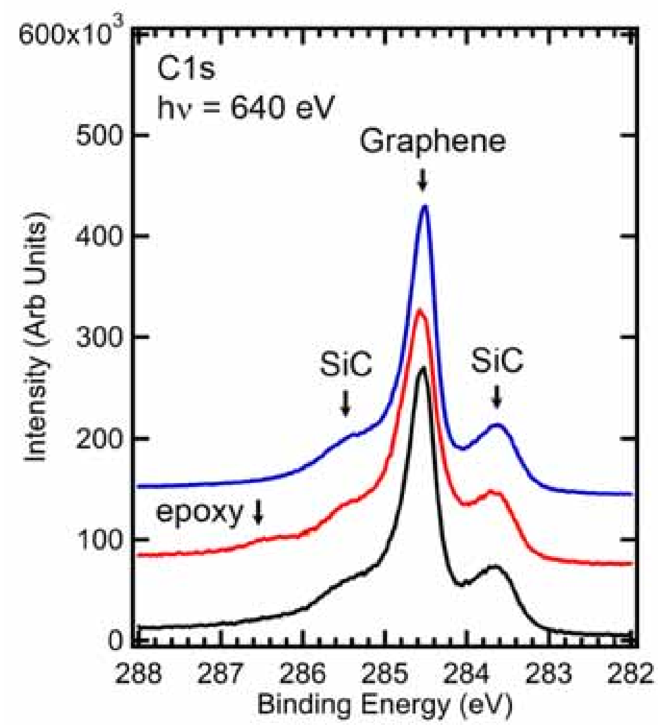


- Oxidation is fully reversible upon thermal annealing or STM lithography.

X-Ray Photoelectron Spectroscopic Verification

Nature Chemistry, **4**, 305 (2012).



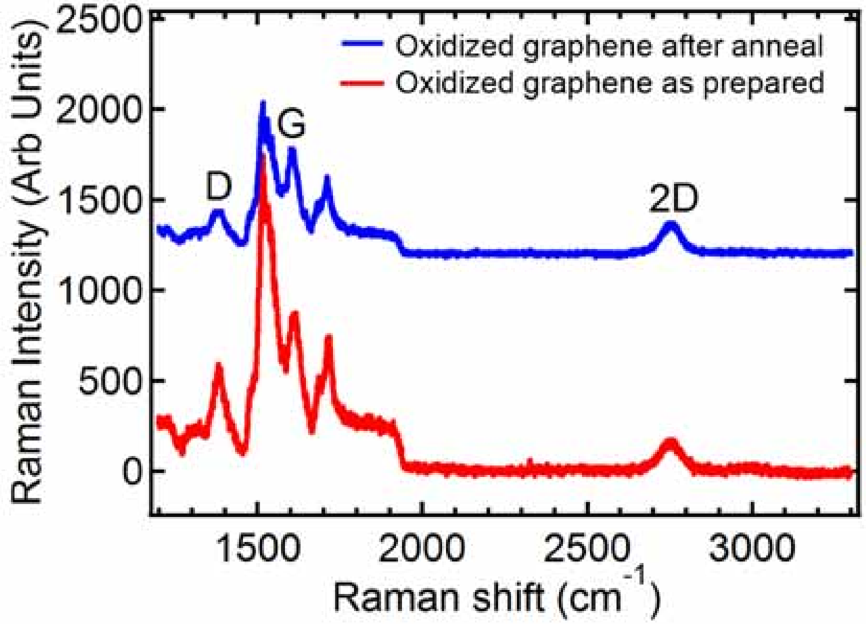


- O1s peak clearly illustrates the reversibility of the UHV oxidation process.
- C1s shoulder at 286.3 eV is indicative of epoxy functionalization.

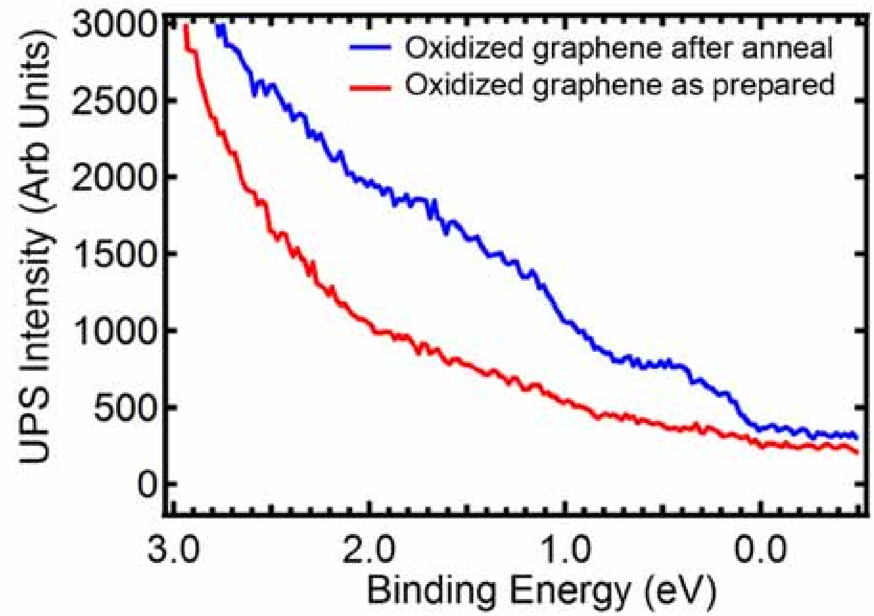
Raman and Ultraviolet Photoelectron Spectroscopy

Nature Chemistry, **4**, 305 (2012).

Raman Spectra



UPS Spectra

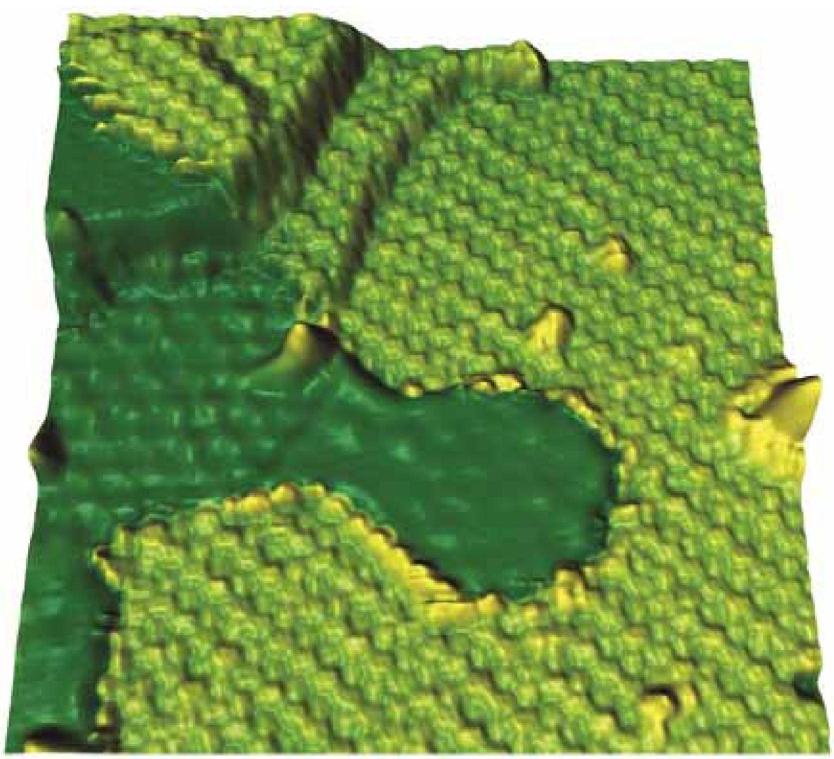


- Raman: D/2D ratio increases after oxidation and reduces following anneal.

- UPS: Electronic density of states decreases after oxidation and increases following anneal, suggesting modification of the electronic band structure.

Outline

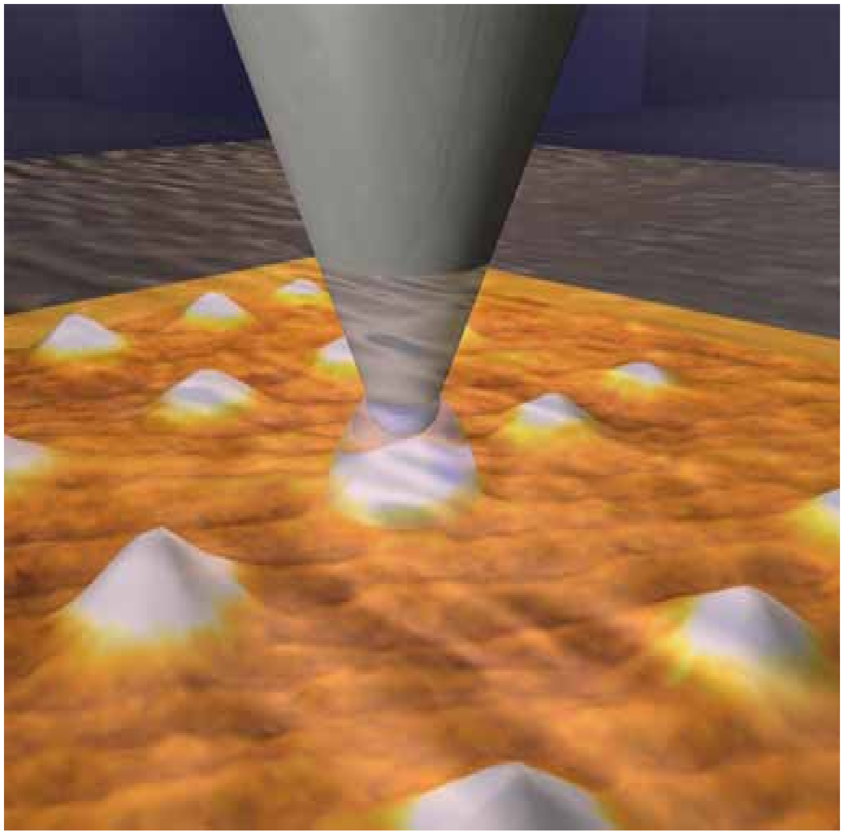
Review Article:
MRS Bulletin, **36**, 532 (2011).

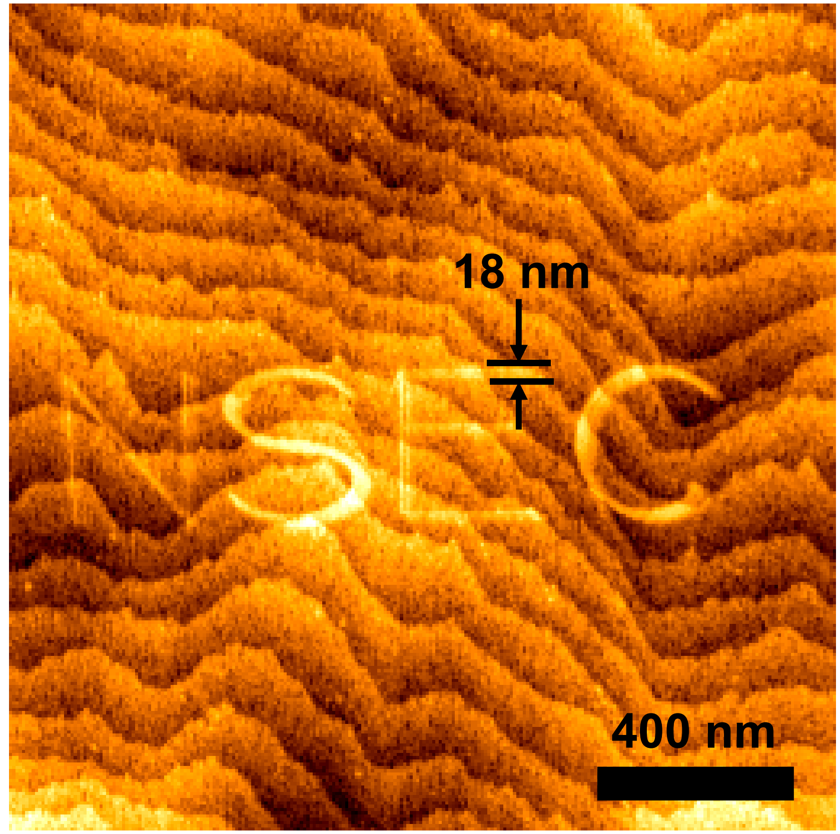


- Weakly interacting organic monolayers on graphene
  - PTCDA
  - Seeding layer for ALD
- Strongly interacting organic and inorganic adsorbates on graphene
  - PTCDI-C8
  - Organic free radicals
  - Atomic oxygen
- Nanopatterning on graphene
  - Nanoscale oxidation
  - Molecular heterostructures

Nanoscale Oxidation with cAFM

Nano Letters, **5**, 91 (2005).

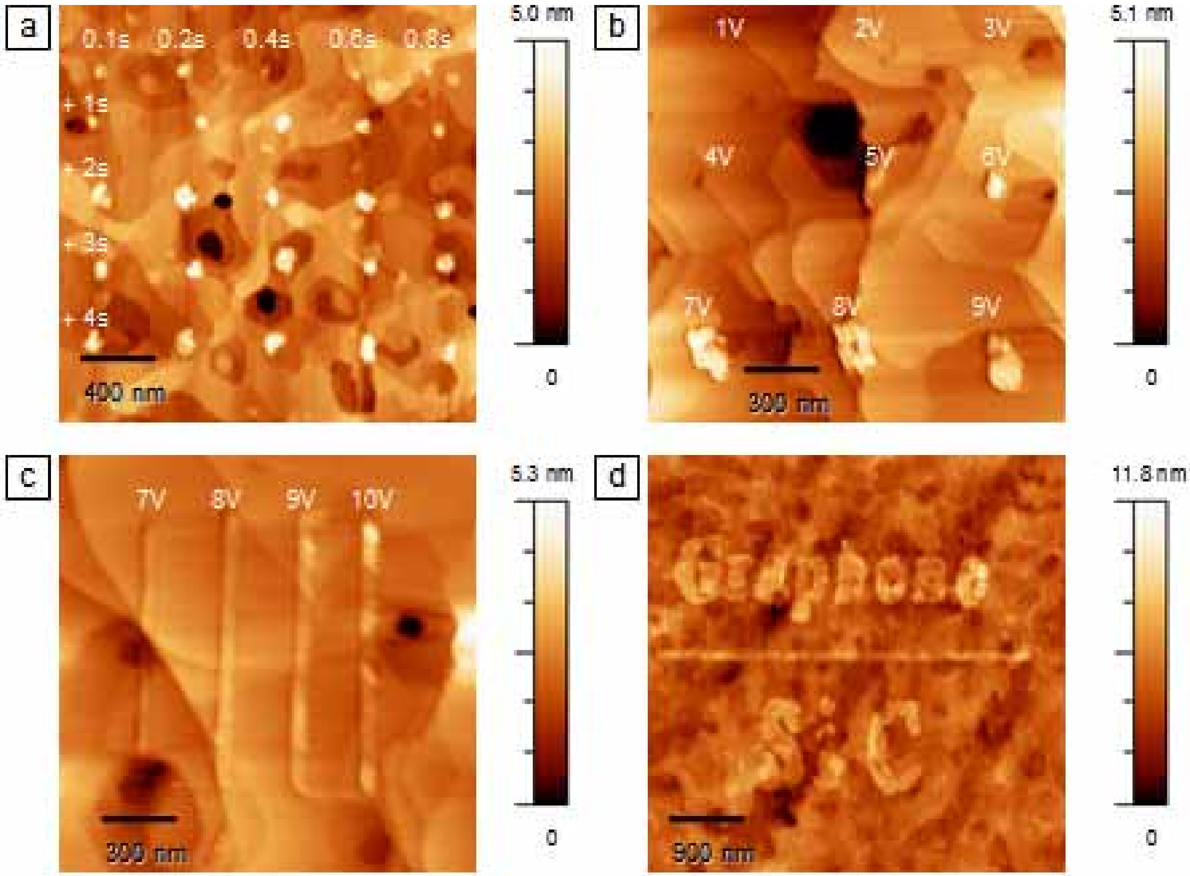




Local anodization of silicon surfaces via conductive atomic force microscopy (cAFM) in ambient conditions

Nanoscale Oxidation of Graphene with cAFM

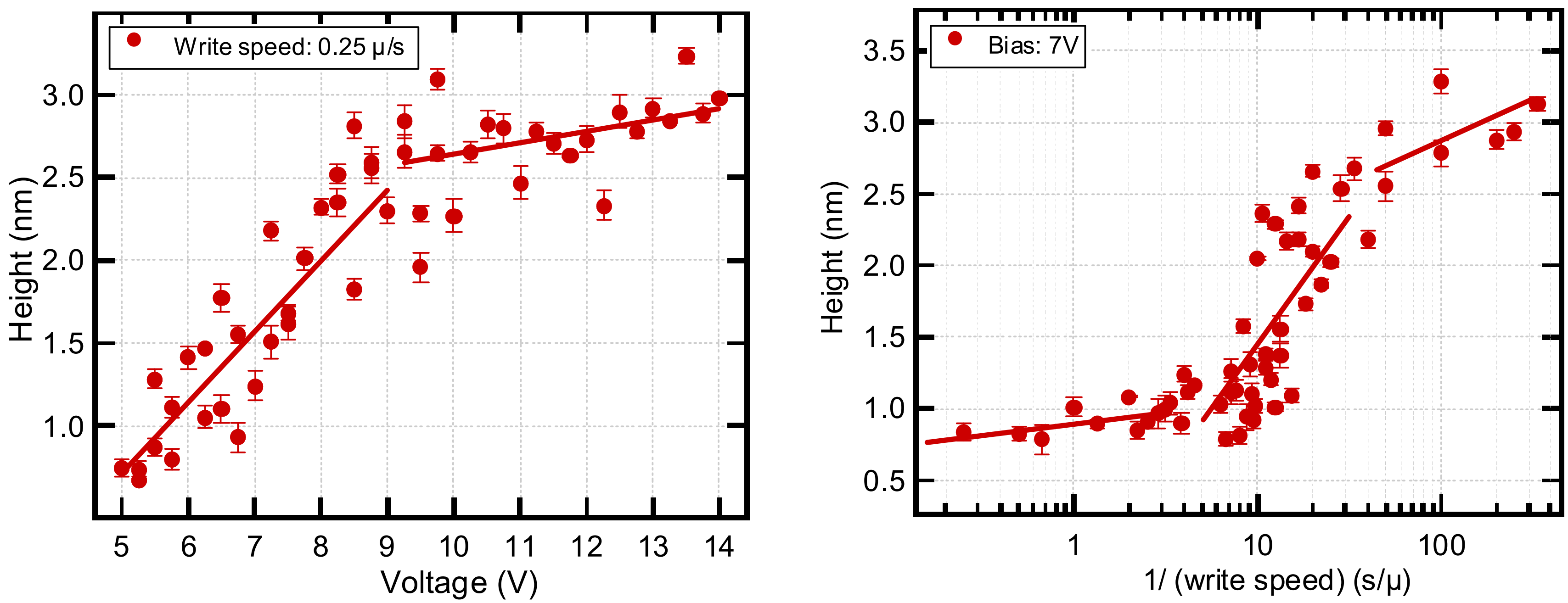
Advanced Materials, **23**, 2181 (2011).



Controllable nanoscale patterns generated on epitaxial graphene under ambient conditions using conductive AFM

Nanopattern Growth Kinetics

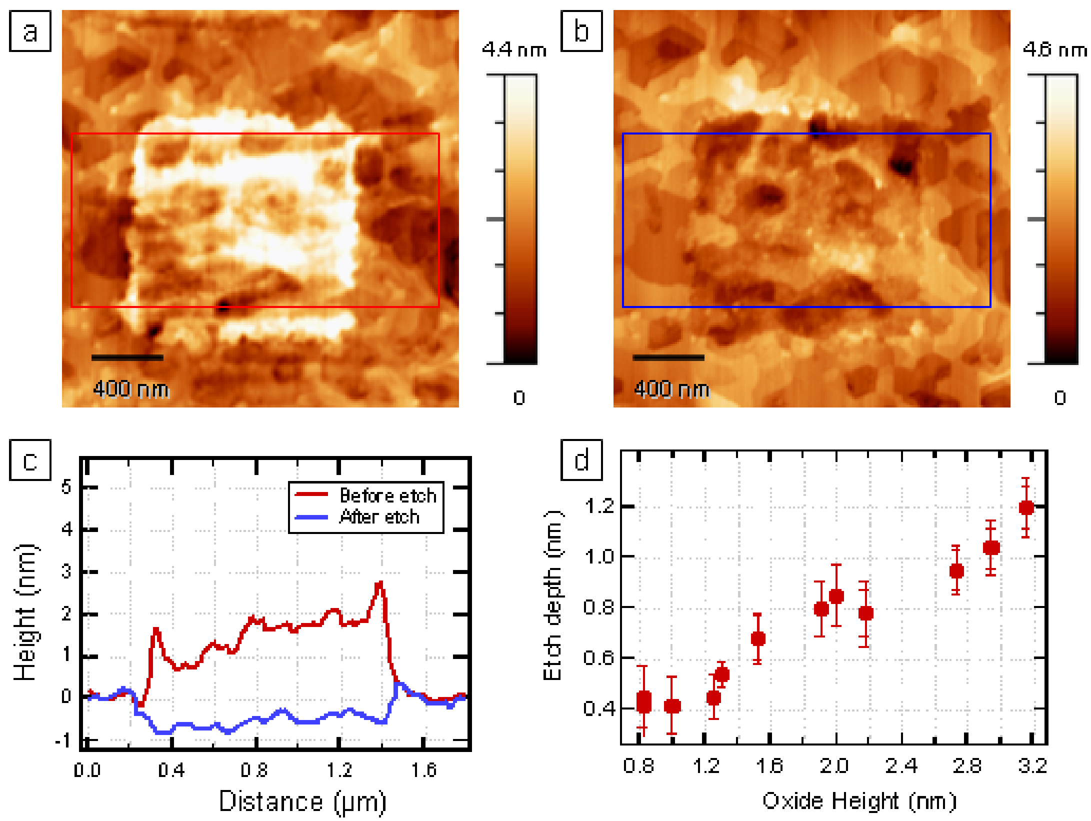
Advanced Materials, **23**, 2181 (2011).



- The kinetics data show distinct regimes of nanopattern height variation with growth conditions.
- The observed distinct regimes are attributed to the non-homogenous depth profile of epitaxial graphene on SiC (i.e., graphene, 6√3, bulk SiC)

Selective Etching in HF

Advanced Materials, **23**, 2181 (2011).



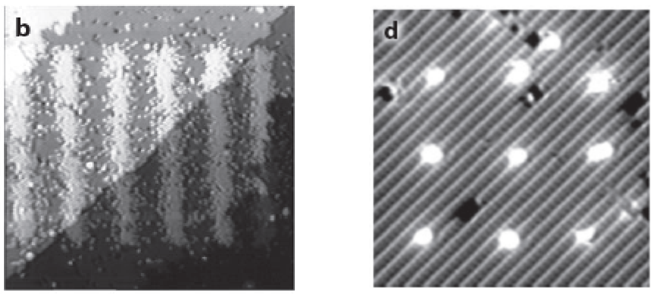
• HF selectively etches nanopatterns with no apparent damage to graphene.

• Etch depth vs. original height has distinct regimes, again reflecting the layered structure of epitaxial graphene on SiC.

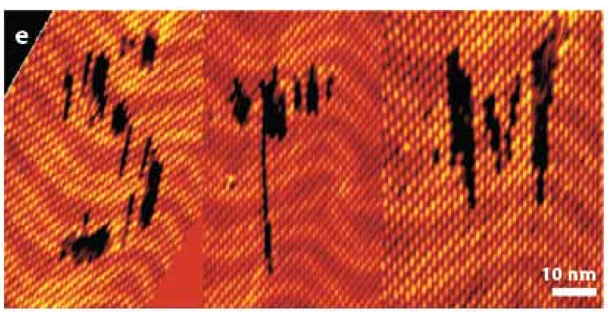
Nanopatterning with UHV STM

Annual Review of Physical Chemistry, **60**, 193 (2009).

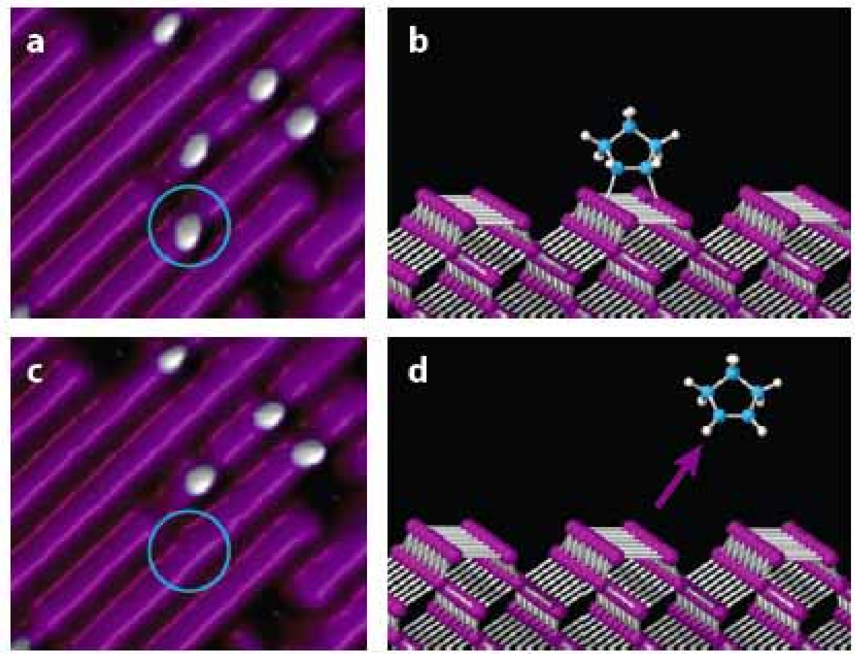
Hydrogen on Si(100)



SAM on Au(111)



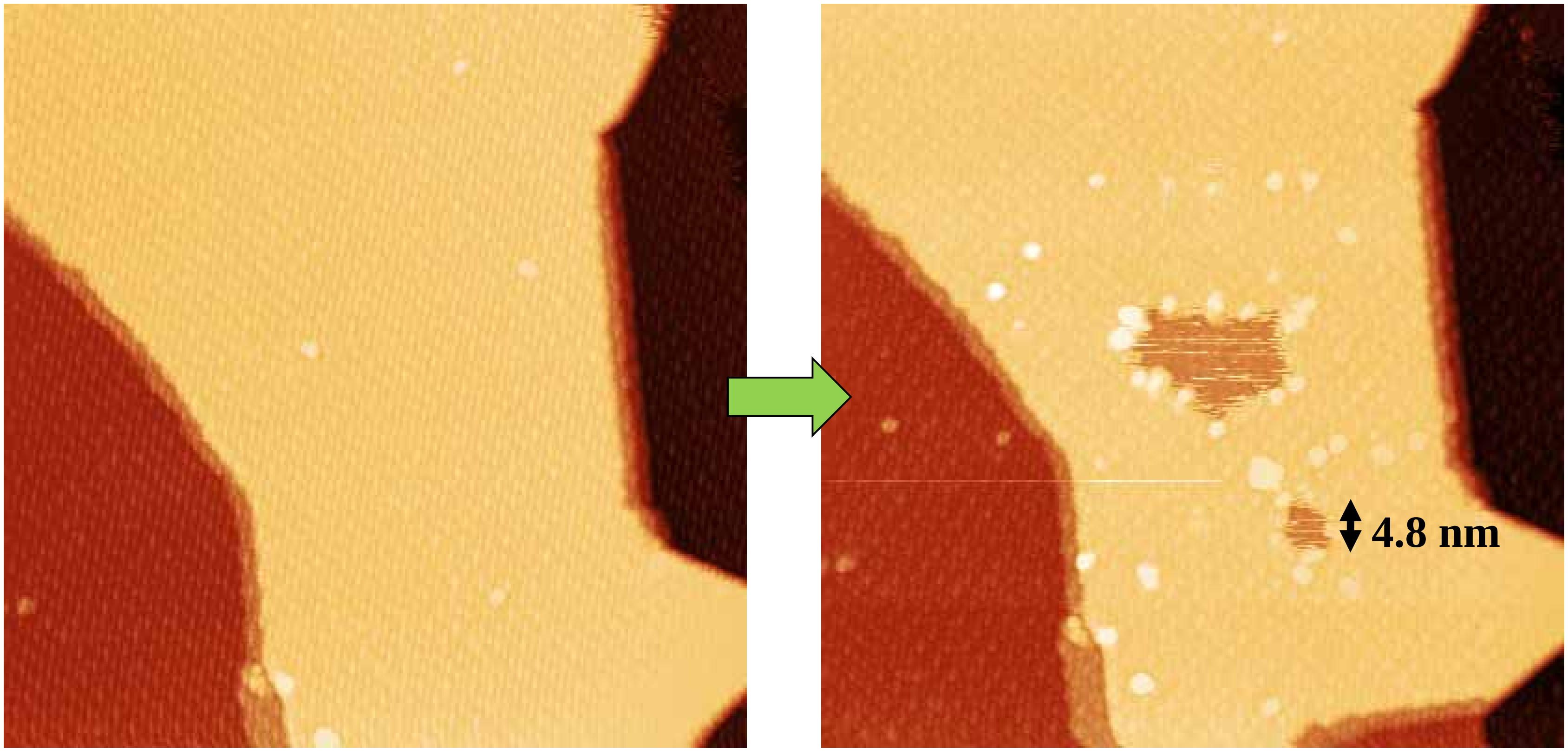
Cyclopentene on Si(100)



- STM can be used to pattern variety of chemical resist layers and isolated molecules
- Tip-induced desorption via electronic excitation or vibrational heating

Nanopatterning PTCDA on Epitaxial Graphene

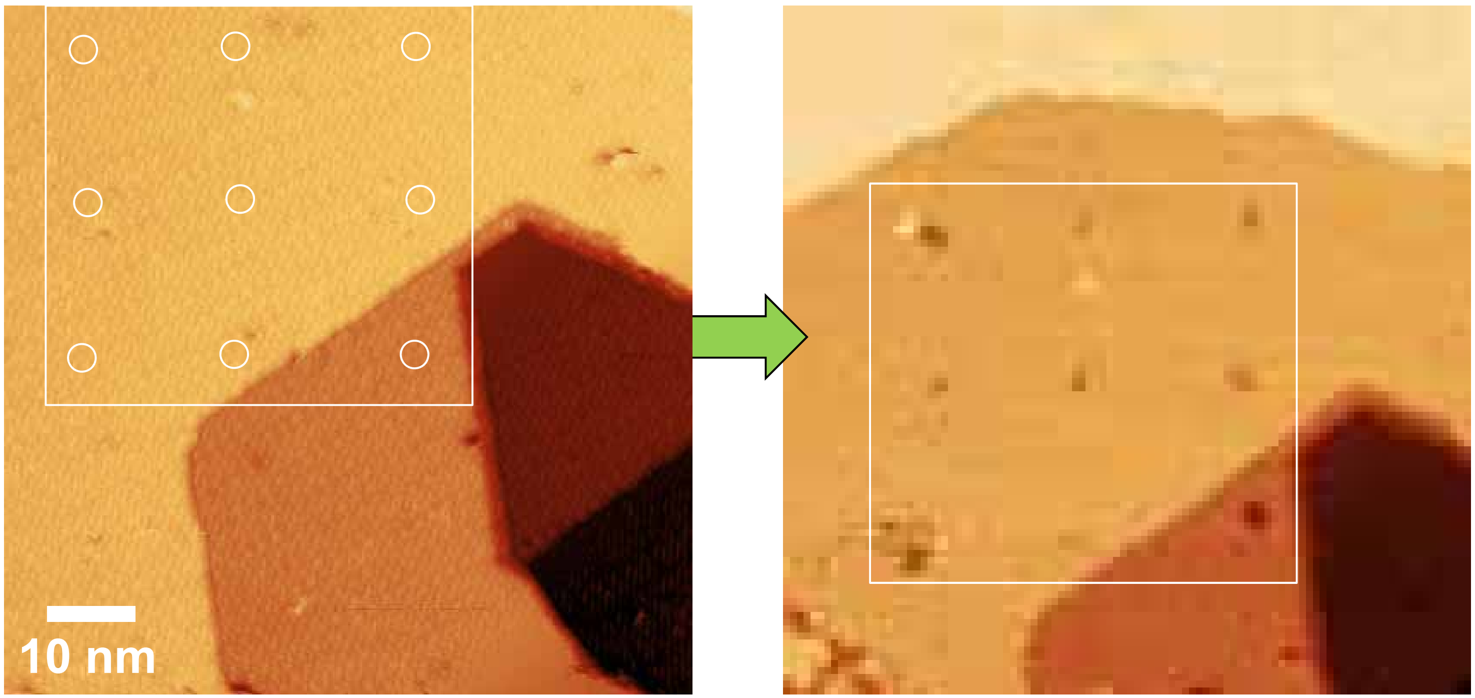
Nano Letters, **11**, 589 (2011).



- PTCDA can be selectively removed with STM voltage pulsing
- Sub-5 nm features possible but inconsistent, probably due to strong intermolecular forces in the PTCDA monolayer

Feedback Controlled Lithography of PTCDA

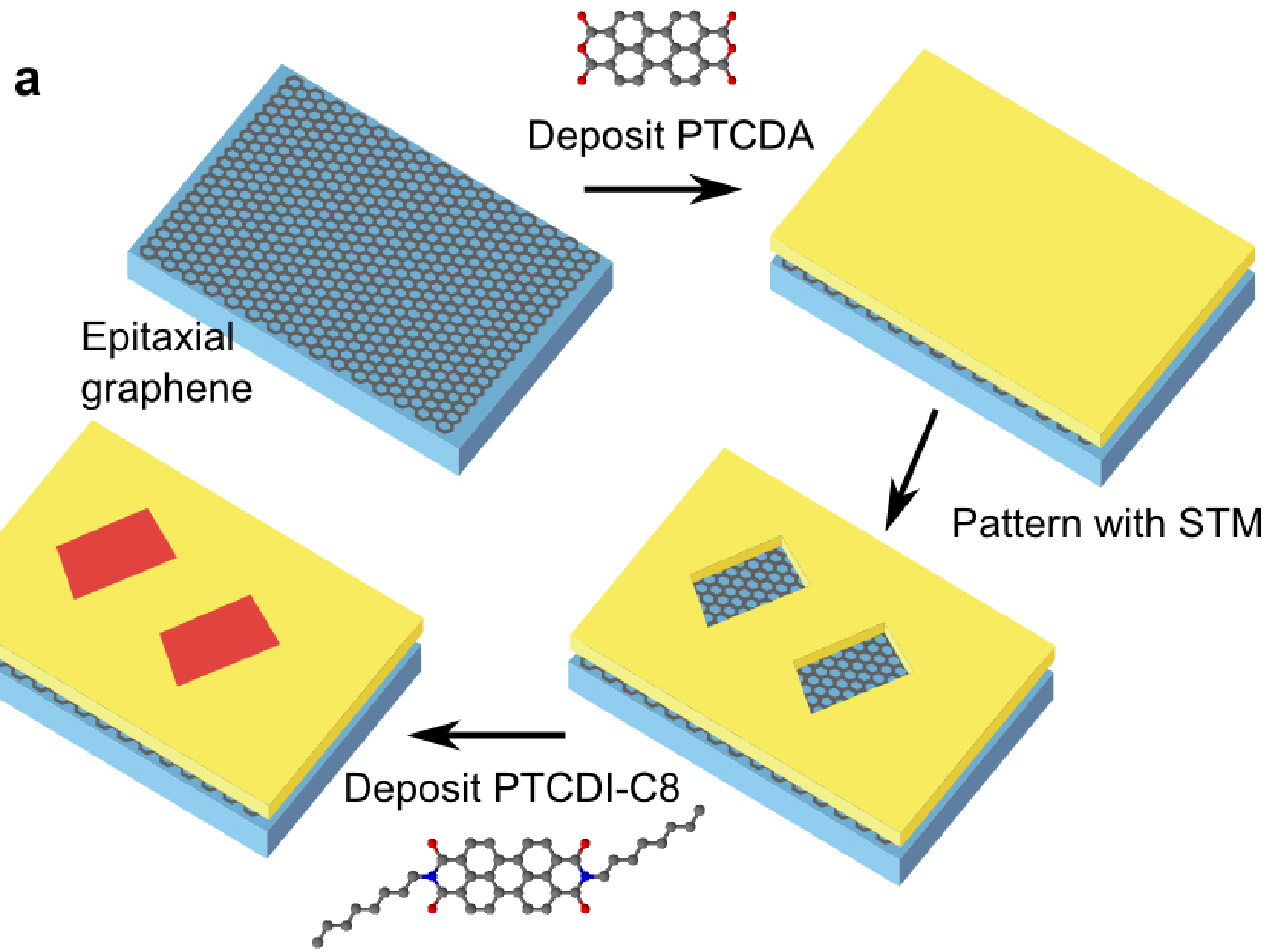
Nano Letters, **11**, 589 (2011).



- Control and reproducibility of patterns greatly improved by using feedback controlled lithography to selectively desorb PTCDA domains that are ~2 nm diameter

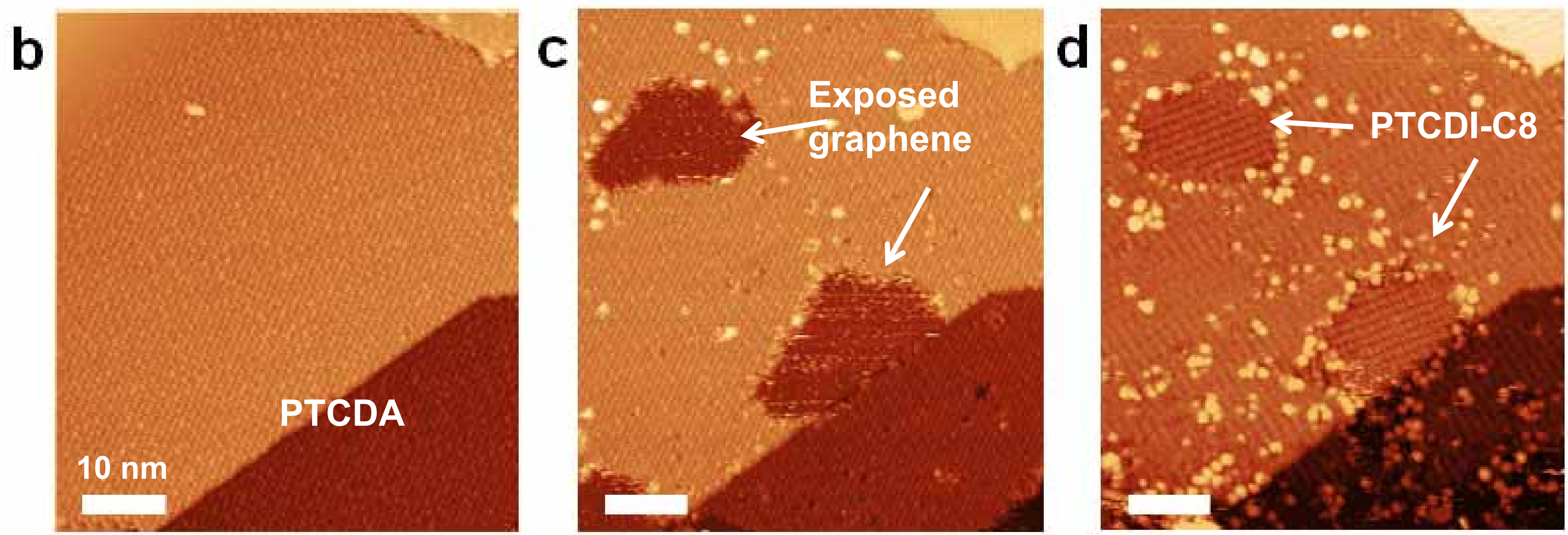
PTCDA as a Chemical Resist on Graphene

Nano Letters, **11**, 589 (2011).



Heteromolecular Nanopatterns on Graphene

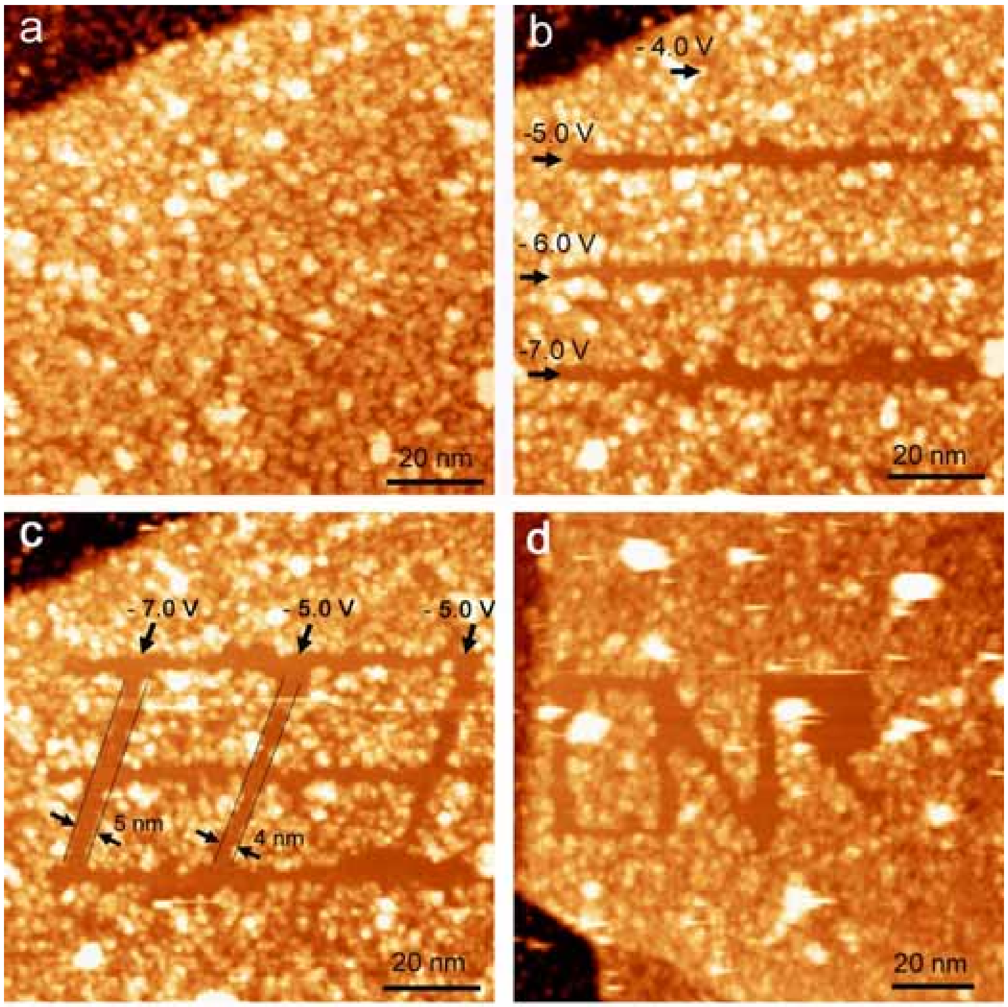
Nano Letters, **11**, 589 (2011).



- Heteromolecular nanopatterns implemented with PTCDA resist and PTCDI-C8 insert
- Molecular ordering is observed in the PTCDI-C8 nanopatterns

Nanopatterning Covalently Modified Graphene

Journal of the American Chemical Society, **132**, 15399 (2010).



- Aryldiazonium chemistry can also be used as a resist for UHV STM nanopatterning
- Threshold parameters: V_{sample} = - 5 V; I = 1 nA
- Nanoribbons with sub-5 nm width reproducibly patterned
- Writings parameters have little to no effect on width

Summary

- Noncovalent organic functionalization imparts uniform chemical functionality with minimal perturbation to underlying graphene.
- Radical-mediated chemistry enables covalent grafting to graphene.
- Electron and photon driven nanopatterning has been achieved down to the molecular scale on graphene.

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