The Radical Atom: Mechanosynthetic 3D Printing of an Atomically Sharp SPM Tip

EE0008308

University of California, Los Angeles and Nanofactory CBN, Inc.

Summer 2018 – Spring 2020

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University of California, Los Angeles

U.S. DOE Advanced Manufacturing Office Program Review Meeting
Washington, D.C.
July 17-19, 2018

Overview Slide

Timeline:

- Award in process
- Anticipated start date – July 2018
- No costs incurred to date

Budget:

	Year 1 Costs	Year 2 Costs	Total Planned Funding (Summer 2018 – Spring 2020)
DOE Funded	$500K	$500K	$1M
Project Cost Share	$125K	$125K	$250K

Barriers:

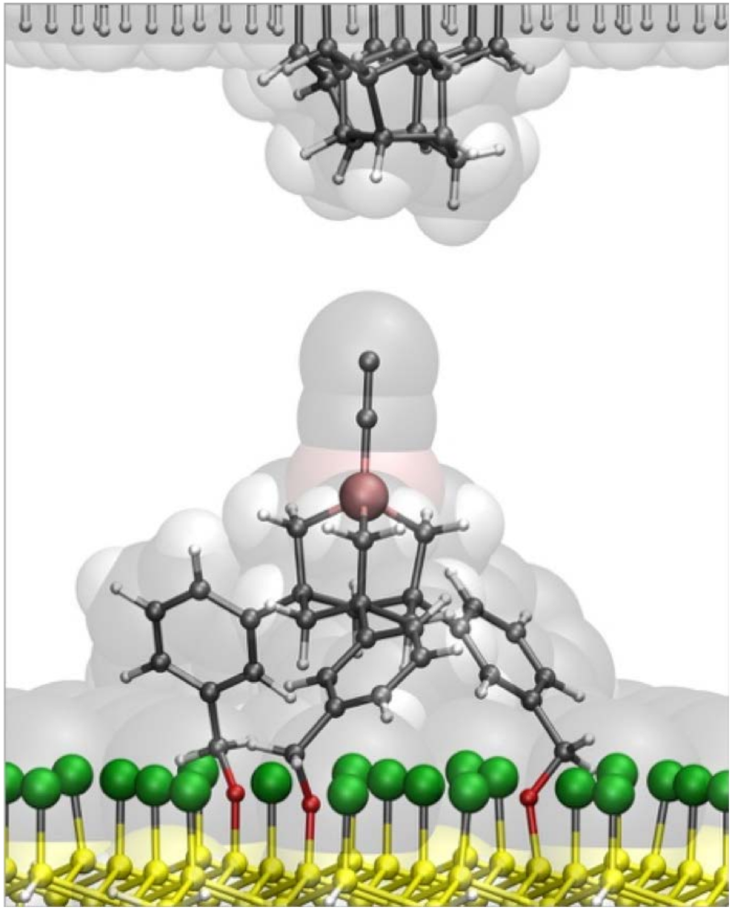
- Key barriers to demonstration of APM technology have been defined by 23 milestones based on 6 programmatic Tasks as seen on slide 9

Partners:

- This program is hosted by the California NanoSystems Institute (CNSI) at the University of California, Los Angeles (UCLA)
  - PI (Gimzewski) and co-PI (Stieg)
- Nanofactory CBN, Inc. serves a sub-awardee to UCLA
  - Lead (Barton)

Project Objectives

In alignment with MYPP Goal 5.4, this project strives to develop a sustained program to design and construct nanosystems for automated, programmable, atomically precise manufacturing (APM) using additive positional assembly.



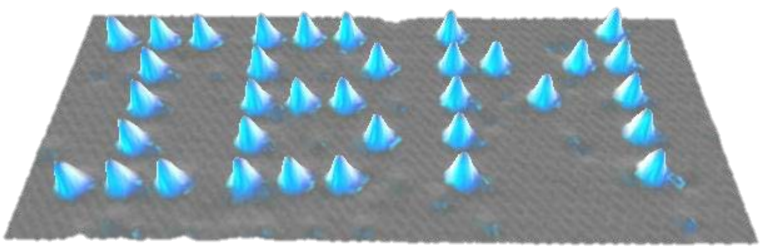
1. Design, synthesize and characterize surface-bound reactants as test structures for APM
2. Demonstrate the ability to re-shape the apical structure of the SPM tip by reproducible and sequential removal of atoms through mechanochemistry

OUTCOME. Success will represent a foundational breakthrough toward 3D tip-based fabrication of atomically precise structures, enabling production of custom catalyst designs, biosensors, thermodynamically limited chemical separation technologies, high-efficiency battery electrodes, post-Moore conventional and quantum computational devices, and all other application areas of chemical and materials science.

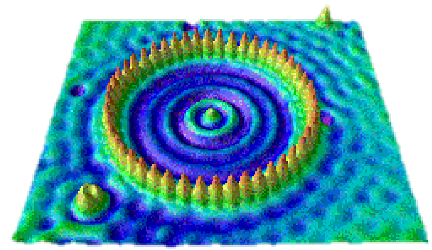
Technical Innovation

STATE OF THE ART.

Current approaches to atomic scale fabrication are typically limited to two-dimensions and rely on either resource intensive techniques such as SPM, FIM, ion milling etc. <u>or</u> self-assembly involving a delicate balance of subtle chemical phenomena.



Eigler, 1989



Eigler, 1993

Gimzewski, 2002

OUR APPROACH.

We will validate an enabling concept for atomically precise manufacturing (APM) utilizing ***mechanochemistry*** to selectively extract or deposit atoms from/to the tip of an SPM to achieve atomically precise control over its apical structure. Computational modeling and chemical synthesis combined with upgrades to existing instrumentation will enable fundamental developments in both tip and surface chemistry to produce surface-bound reactants for re-shaping matter with atomic precision in three-dimensions.

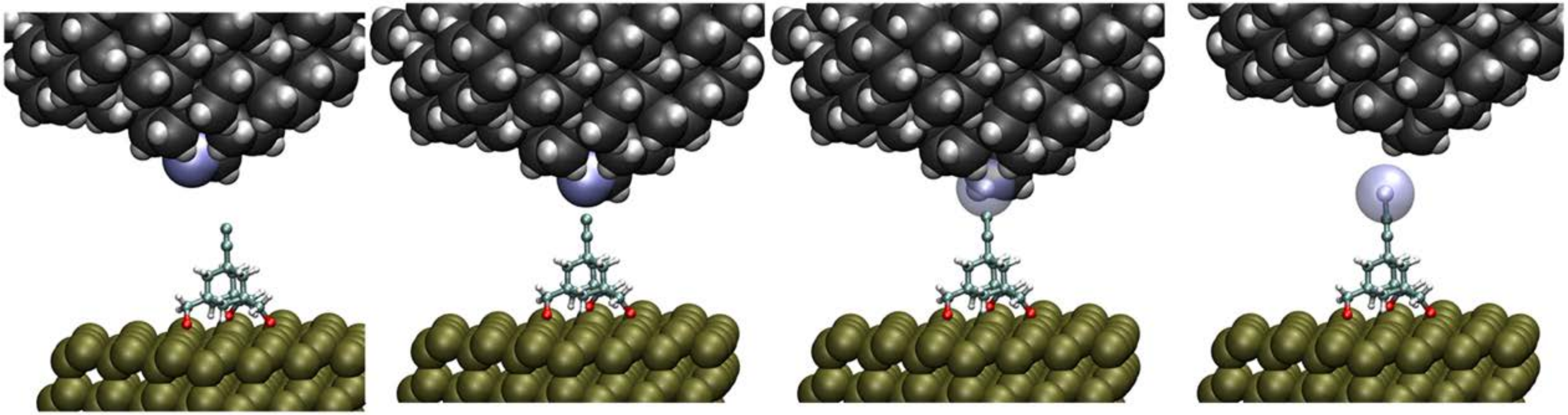
IMPACT.

A general method for generating reproducible tip structures will revolutionize the field of SPM-based APM, opening the door to positional control of nearly arbitrary covalent chemistry in three dimensions. **In the short term, this allows the SPM community to work with reliable tips of known structure. In the medium term, this allows us to build 3D structure using known tips. In the long term, this allows us to build an APM future.**

Technical Innovation

Mechanochemistry.

Applying mechanochemistry to tip modification is conceptually straightforward: create a high-energy reactive molecule on the surface, approach the tip atom you want to remove to that molecule, make a bond to the tip atom, and pull away to remove the atom from the tip.

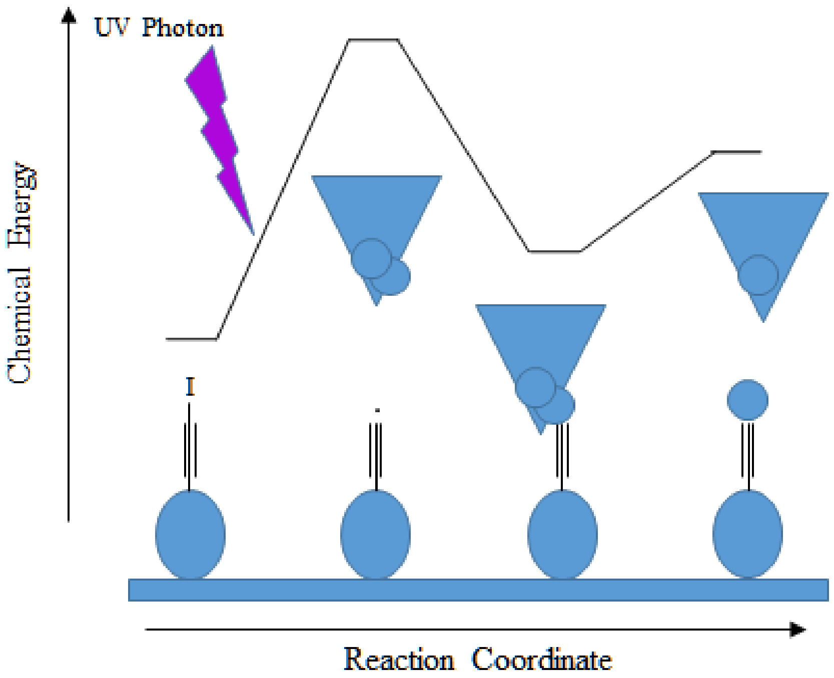


Proposed mechanochemical reaction. Computational depiction of atomic abstraction of a defect from the apex of a silicon SPM tip. From left to right, defective tip scans abstraction molecule, defective tip approaches with extraction molecule, abstraction molecule reacts with defective tip, reactive molecule pulls defect atom from SPM tip.

Technical Innovation

Surface-bound radicals.

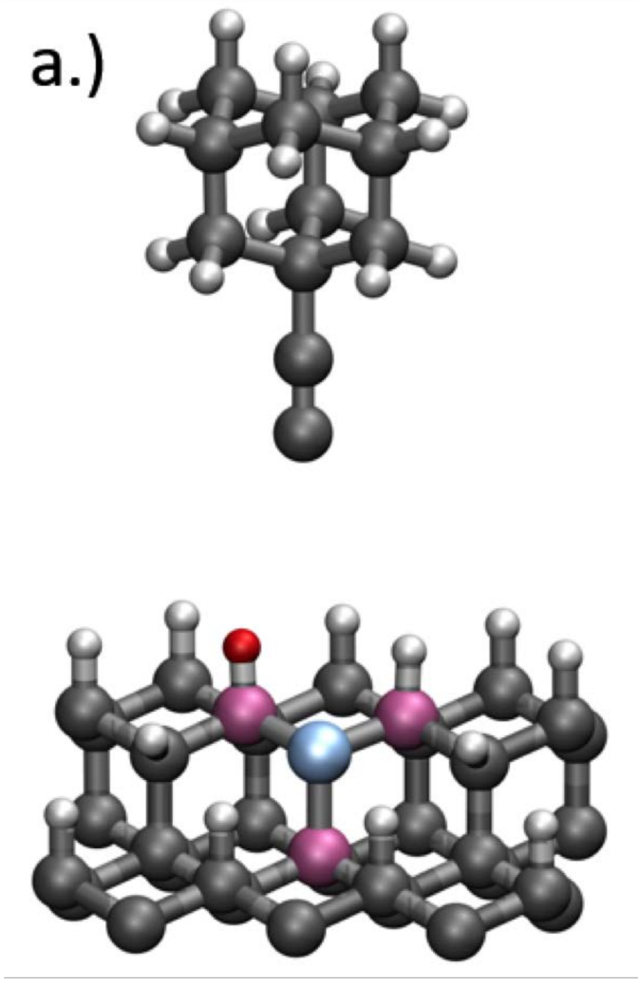
Creating a reliable system for removing atoms from the tip will require an asymmetric chemical potential between the tip and the molecule it is reacting with. Photolytic generation of radicals creates such a potential between the tip and the surface-bound reactant molecule. If the system is symmetric, pulling away will break a random bond. If a system has a single weak link, that is where it will most likely break. This proposal is built around ensuring that the weak link is the chemical bond between unwanted tip atoms and the tip itself.



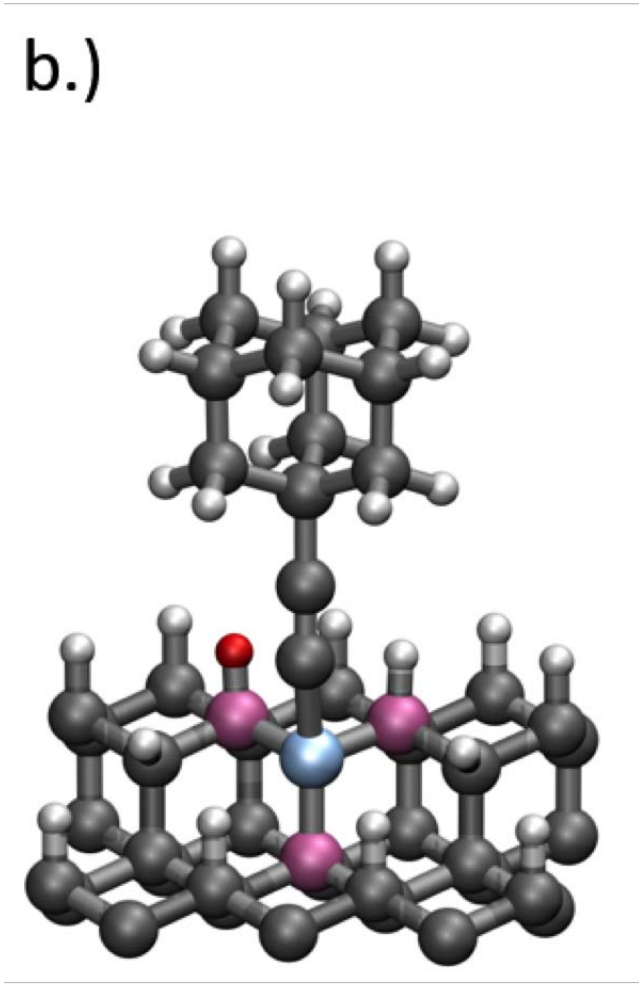
An example surface presenting a C2-I. Photolysis generates a C2* which interacts with the SPM tip, reducing the free energy and interacts strongly with the tip. Retraction leads to abstraction of an atomic/molecular component from the tip, increasing the energy but to a level more thermodynamically favorable than the initial condition.

Molecular tool approaches a dehydrogenated C(111) step edge carbon (blue).

DFT calculations indicate favorable reaction.

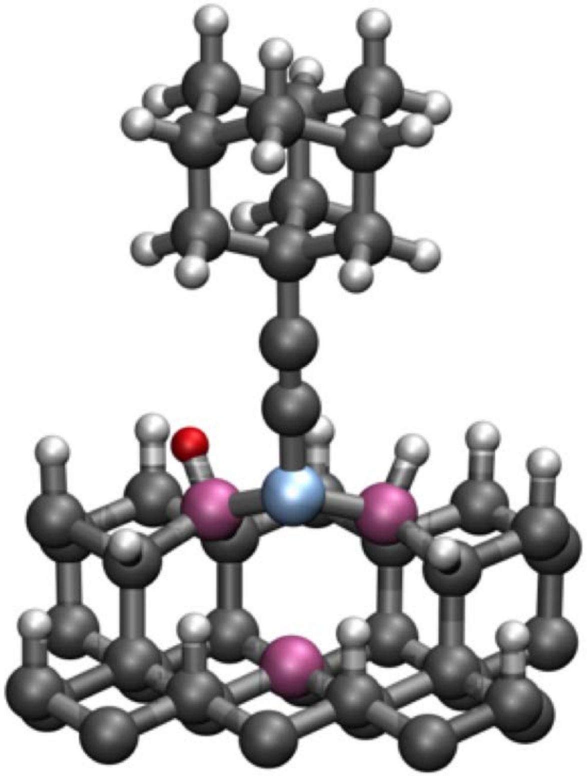


Tool binds to carbon



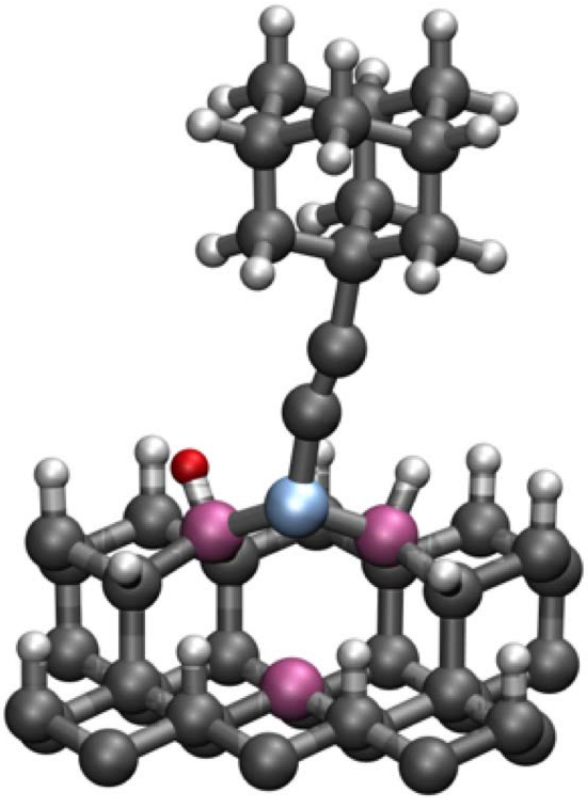
Molecular tool displaced upward, breaking first C-C

c.)



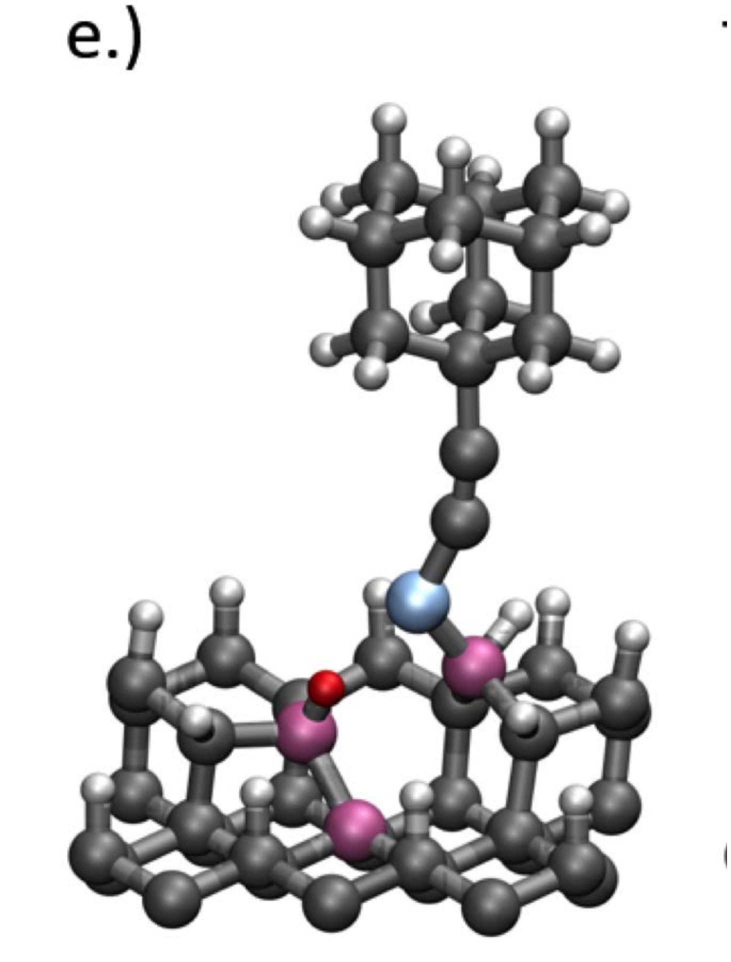
molecular tool is displaced to right
begin breaking second lattice bond

d.)

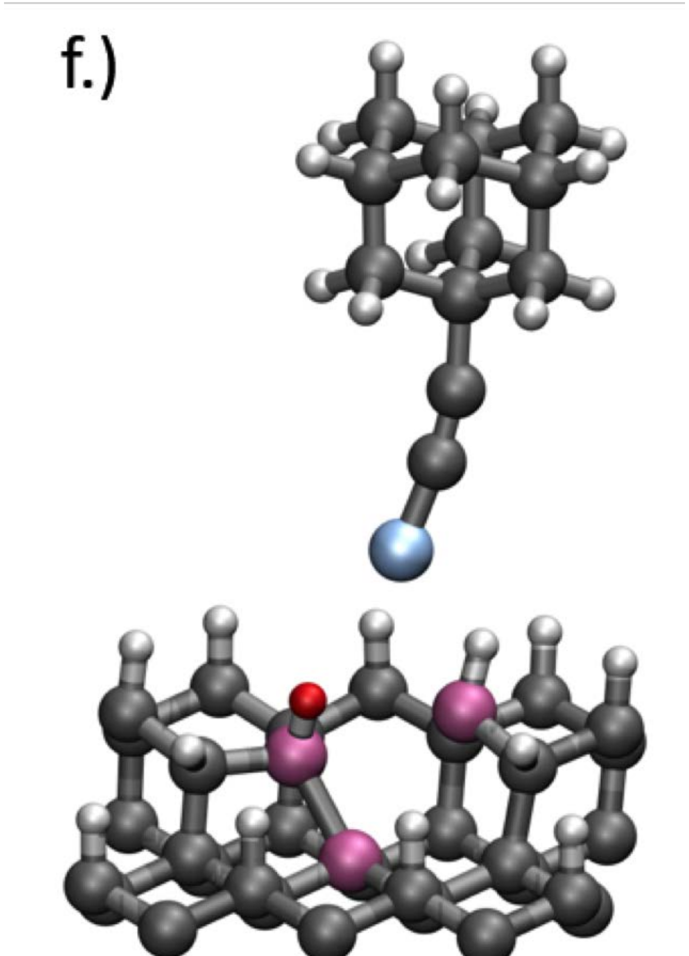


Diamond lattice rearranges to minimize energy of two radicals within the lattice

- Resulting structure represents a new high energy defect addressable by molecular tools

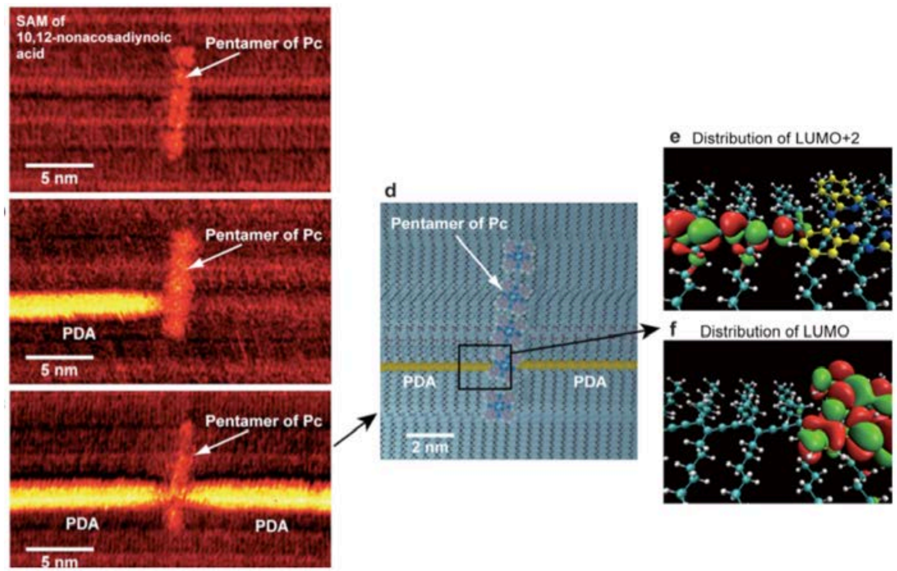


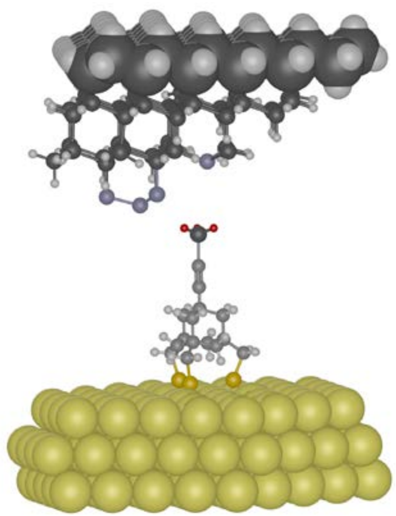
Molecular tool displaced vertically, removing the carbon atom from the lattice



Technical Approach

- The project will integrate computational chemistry and reaction modeling with state-of-the-art, scanning probe-based methods for flexible and scalable 3-D nanofabrication with individual atoms and molecules.





- To mitigate risk, three decision points have been defined:

1. (Q4) Demonstration of activated, surface-bound reactants
2. (Q5) Use of a surface-bound reactant to characterize the apical structure of the SPM tip.
3. (Q6) Demonstration of atom abstraction from the SPM tip through controlled interaction with surface-bound reactants.

Technical Approach

Participant roles and responsibilities:

- UCLA - Gimzewski will take an overall programmatic lead and work closely with Stieg to ensure effective, integrated execution of the proposed research efforts.
- UCLA – Gimzewski will oversee instrument upgrades/development efforts and surface chemistry efforts as well as student/postdoctoral mentorship.
- UCLA – Stieg will lead instrument upgrades/development and tip chemistry efforts.
- Nanofactory CBN, Inc. – Barton will lead the computational, synthetic, and mechanosynthetic chemistry efforts.

Attributes of the team:

- Gimzewski is a recognized leader in SPM methods, having published over 250 papers in the field over the last 30 years, including the first STM-based fabrication of molecular suprastructures using mechanical forces.
- Stieg provides over 15 years of experience in the development and application of advanced SPM instruments and methods.
- Barton has spent the last six years at Nanofactory CBN, Inc. directing the development of practical approaches to APM.

Results and Accomplishments

The program has not yet started. An overview of tasks is as follows:

Task	Milestone	Date	Location
1 – Target Definition	Select tip material(s), substrate and reactant identity	Q1	Nanofactory CBN
2 – Instrument development	Upgrade and validate existing UHV-SPM for LT-STM/ncAFM	Q1-5	UCLA
3 – Chemical synthesis	Synthesize purified reactants at gram-scale quantities	Q2-3	Nanofactory CBN
4 – Surface chemistry	Demonstrate reactant chemisorption and activation	Q3-4	UCLA
5 – Computational modeling	Simulate, model and refine tip—sample reaction trajectories	Q1-8	Nanofactory CBN
6 – Tip chemistry	Demonstrate reactant-driven abstraction/donation of individual atoms to/from the SPM tip apex through mechanochemistry with surface-bound reactants	Q5-8	UCLA

Transition (beyond DOE assistance)

- The fabrication of an APM tool first relies on a atomically defined 3d tip apex both in terms of atomic structure and chemistry.(THIS PROJECT).
- Radical atom chemistry with picometer precision tips will then permit the fabrication of true APM 3d structures on surfaces with designer functionality guided by computer simulation
- Examples include but are not limited **3D atomic printing** of quantum computational component devices, atomic electronics, new catalysts and advanced materials beyond current synthetic routes
- Nanofactory will be involved in development of advanced APM technology capable of generating a platform for the manufacture of structures and systems with ultimate limits of measurement and fabrication of new 3d APM systems and devices
- This path will eventually lead to megafast APM assembly systems with multiple tips focusing on covalently bonded structures at the ultimate limits of fabrication and measurement.
- Use computers power to accurately predict and design smart molecular building blocks unattainable in current manufacturing technology

Questions?