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

EE0008308

University of California, Los Angeles

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University of California, Los Angeles

U.S. DOE Advanced Manufacturing Office Program Review Meeting

Washington, D.C.

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One of five coordinated 1465 FOA projects in Atomically Precise Manufacturing.

Overview

As next-generation technologies for electronic, photonic, and mechanical devices approach the atomic scale, it is crucial to develop methods for atomically precise manufacturing (APM). A persistent hurdle in the application of nanotechnology to manufacturing is our inability to practically realize atomically defined structures. ***The Radical Atom*** aims to develop a new approach to robust and scalable manufacturing on an atom-by atom basis in three-dimensions.

Timeline:

- Award initiated - August 2018
- Team re-organization - January 2019
- Budget revision under review - March 2019
- No-cost extension request for Budget Period 1 in process – May 2019
- New project end data – December 2020

Budget:

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

Barriers:

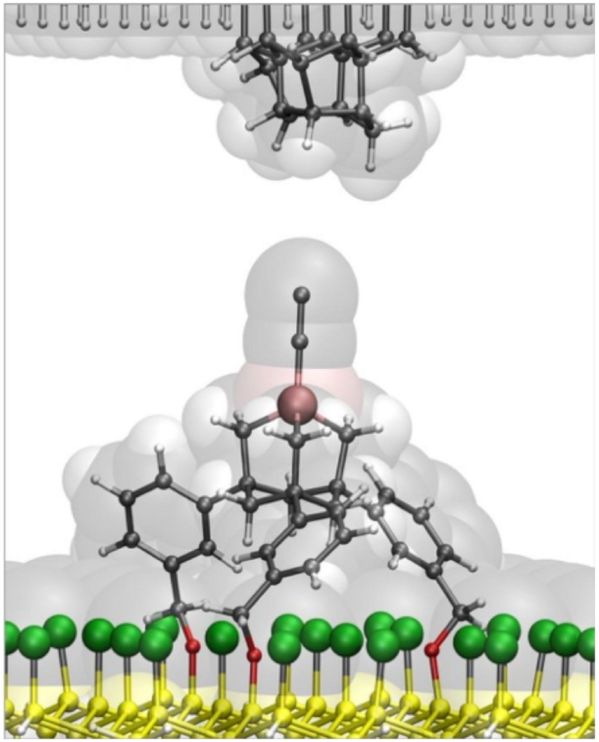
- 30 years of instrument development will be leveraged to overcome the limits of positional control in 3D w/ atomic precision.
- Designer molecular tools (radicals) will enable the spatially-defined formation and/or rupture of individual atomic bonds.

Partners:

- This program is hosted by the California NanoSystems Institute (CNSI) at UCLA
  - Gimzewski (PI) oversees SPM development and surface chemistry efforts (Tasks 2 & 4)
  - Rubin leads synthetic chemistry efforts (Task 3)
  - Sautet leads the computational efforts (Tasks 1 & 5)
  - Stieg leads instrument and tip chemistry efforts (Tasks 2 & 6).

Project Objectives

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



Mechanochemical Assembly

MILESTONES.

To develop a viable platform for APM, ***The Radical Atom*** will:

1. Design and synthesize surface-bound radicals that serve as molecular tools to directly and controllably form/rupture atomic bonds.
2. Demonstrate the fabrication of a scanning probe microscope (SPM) tip that is atomically sharp in three dimensions.

POTENTIAL BENEFITS.

A foundational breakthrough toward direct fabrication of atomically precise structures for applications in:

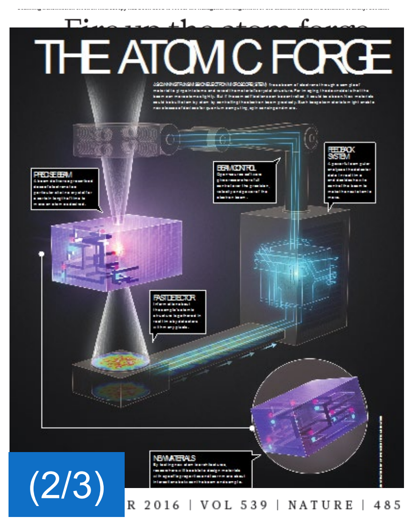
1. Catalysts using low coordination and/or metastable structures leading to low cost manufacturing processes
2. Synthesis of functional molecules and materials with improved reaction specificity and yields
3. Qubit arrays and networks for quantum computation

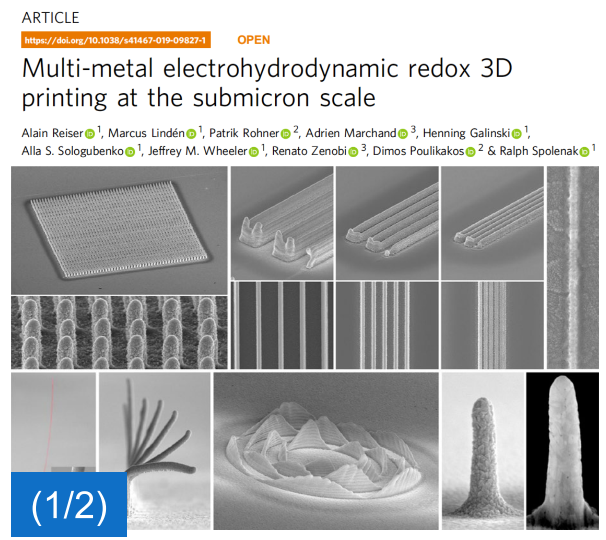
CHALLENGES. Despite dramatic advances in top-down manufacturing and bottom-up assembly at nanoscale dimensions, the precise control over the interactions between individual atoms required for APM in 3D has remained elusive.

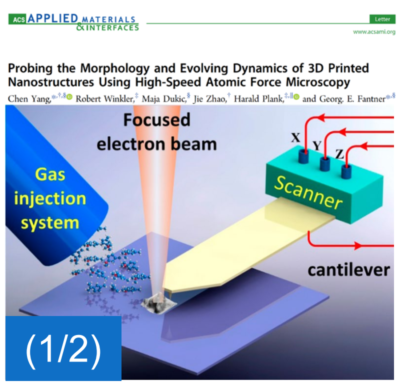
Technical Innovation

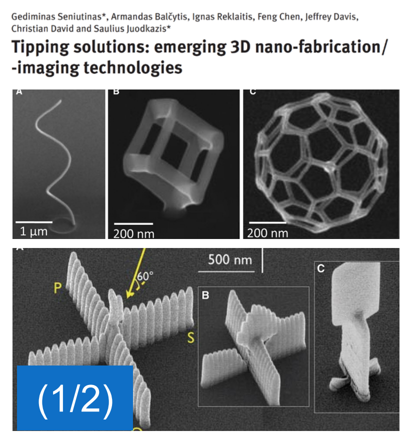
Current state-of-the-art in 3D fabrication at the nanoscale.

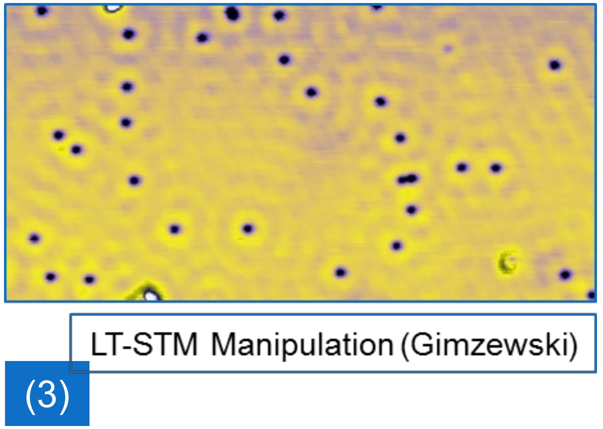
All modern techniques are limited by resolution[1], specificity[2], or dimensionality[3]







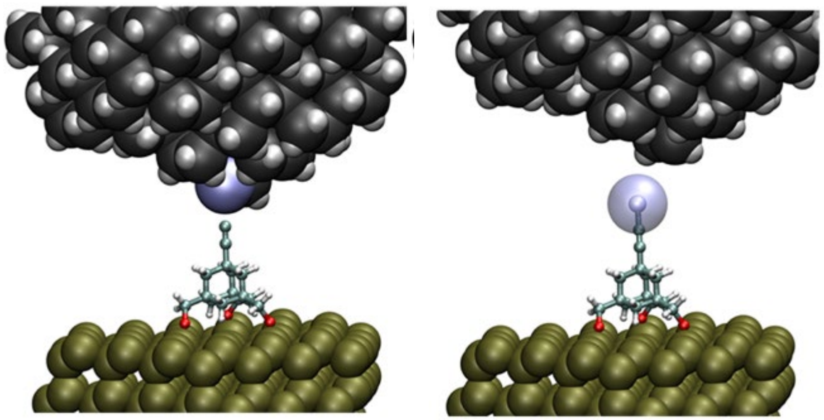




Technical Innovation

(1) Mechanochemistry

Coupling mechanical and chemical processes at the molecular scale

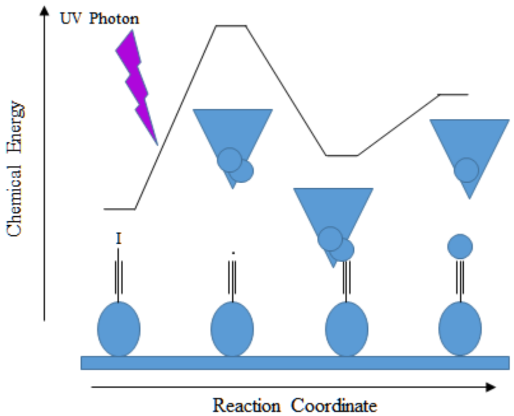


Application to SPM tip modification:

- Create a high-energy, reactive molecule (radical) on the surface
- Approach the tip atom to be removed toward the surface-bond molecular radical
- Make and/or allow for bond formation
- Pull away to abstract the atom from the tip

(2) Molecular radicals

Provide a potential to spontaneously and selectively abstract atoms

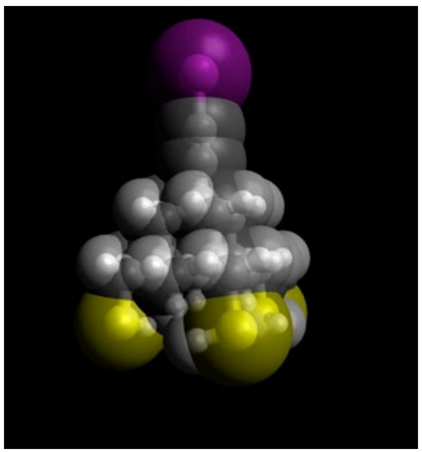


An asymmetric chemical potential between the SPM tip and surface-bound molecular tool (radical) will break an atomic bond at the tip apex, increasing the overall energy to a more thermodynamically favorable level than the initial condition.

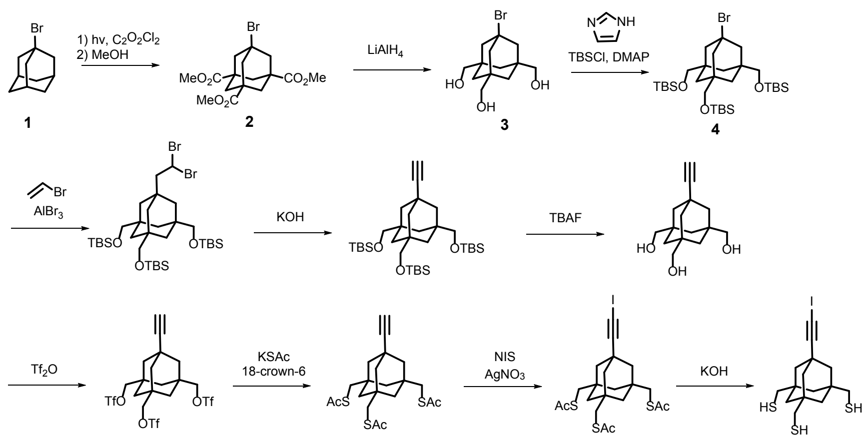
(3) Scalability. An achievable areal density of molecular tools can reach ~10^{12} reactive sites/cm^2, providing nearly infinite repeatability of both additive or subtractive atomic manipulation of material structure in 3-dimensions.

Technical Approach

- The project will integrate computational chemistry (Task 1 - Sautet), organic synthesis (Task 3 - Rubin) and reaction modeling (Task 5 - Sautet) with state-of-the-art, scanning probe-based methods (Tasks 2,4 and 6 – Gimzewski and Stieg) for 3-D nanofabrication with individual atoms and molecules.



Tasks 1 & 5



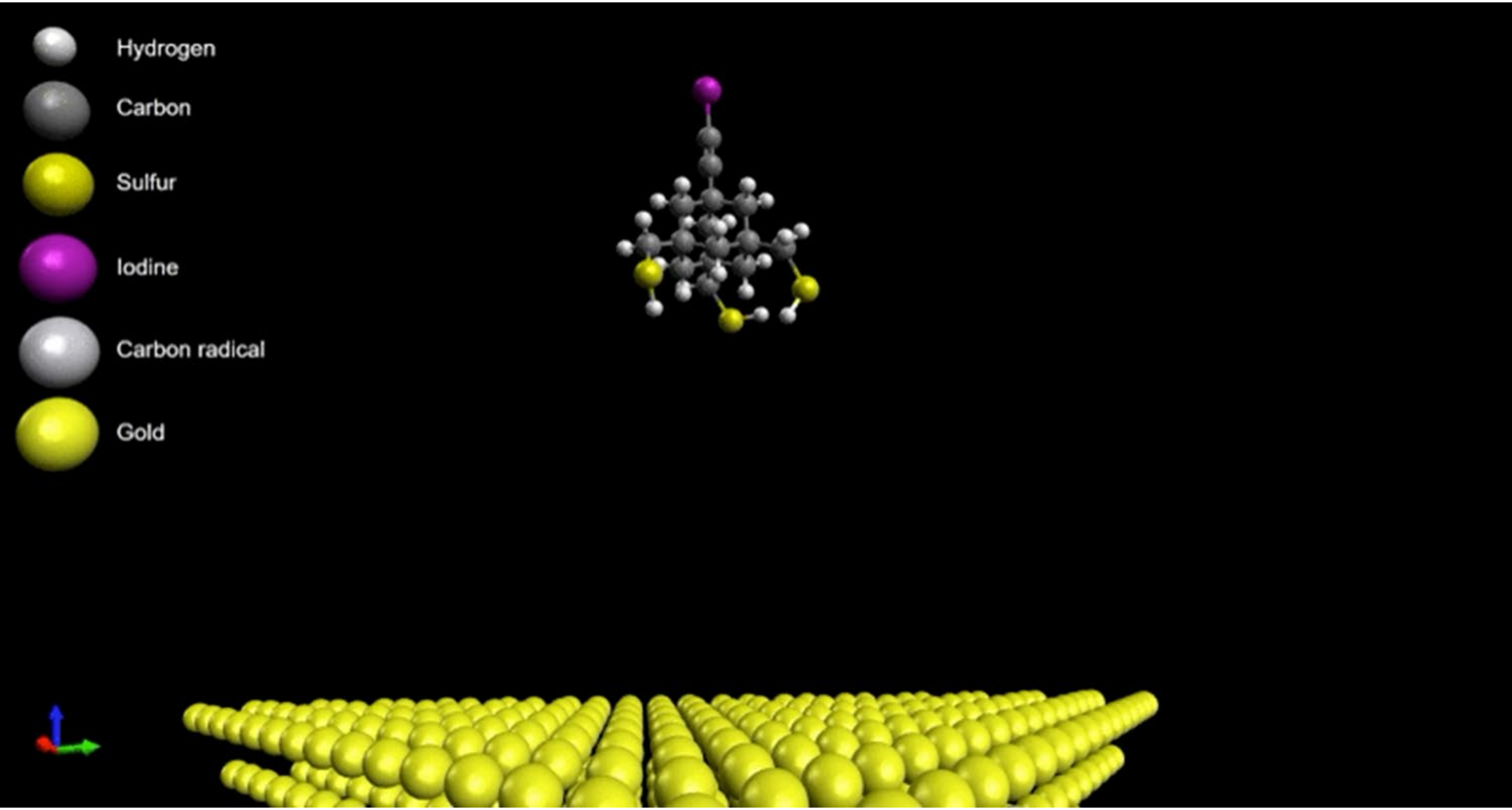
Task 3

Tasks 2, 4 & 6

- 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 structure of the SPM tip apex.
3. (Q6) Demonstration of atom abstraction from the SPM tip through controlled interaction with surface-bound reactants.

Technical Approach

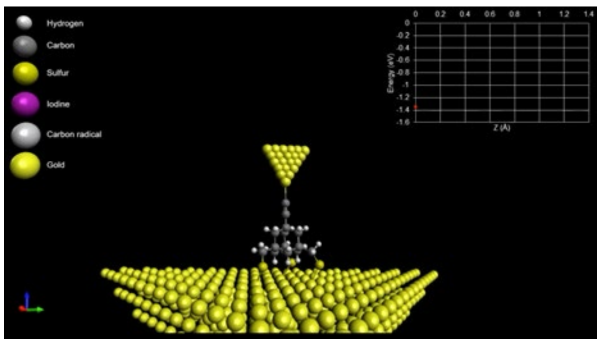


Results and Accomplishments

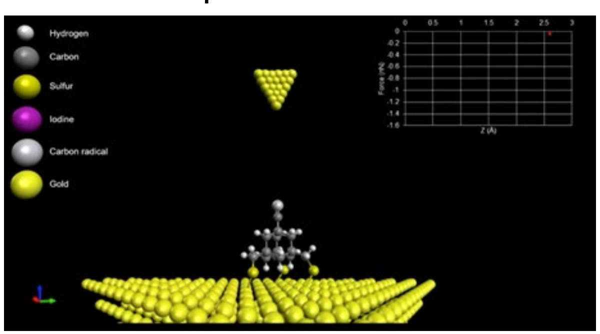
Molecular Design (T1) & Reaction Modeling (T5)

A molecular tool has been designed:

- Trithiol linkage for chemisorption
- Diamondoid core for stability



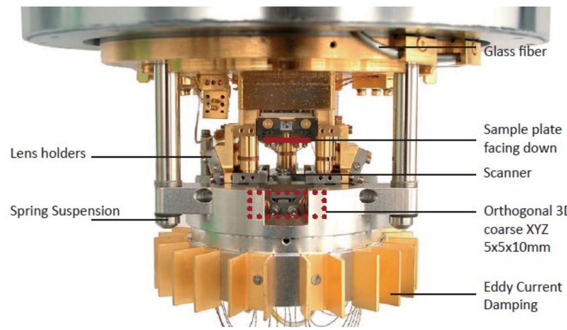
- Activated radical headgroup to abstract atoms from the SPM tip
- Modeling of reaction trajectories to inform experiment



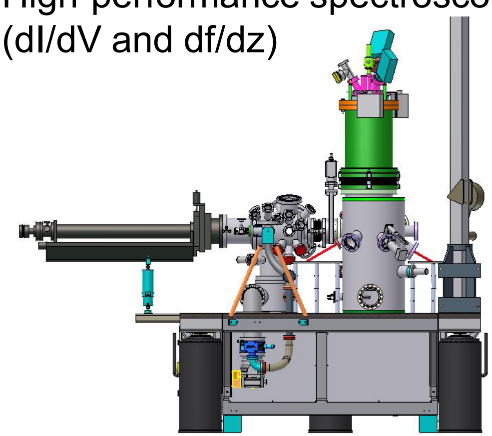
Instrument Upgrade & Development (Task 2)

LT-SPM has been configured:

- <1 pm of drift/hr (1/300th atomic diameter) @ 4K temperature



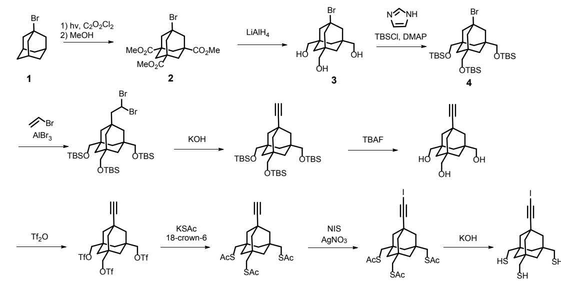
- Simultaneous STM/nc-AFM
- High-performance spectroscopy (dI/dV and df/dz)



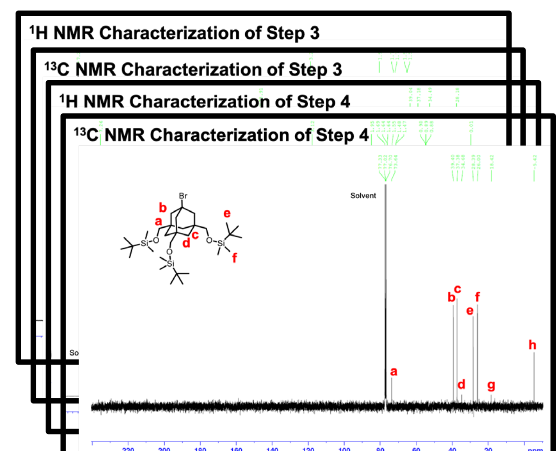
Chemical Synthesis (Task 3)

Synthetic path enables:

- Use of various head (radicals) and anchoring groups



- Scalable production of purified chemical precursors



Results and Accomplishments

Task	Status	Dates	Schedule
1 – Target Definition	Methods have been developed and implemented. Specific molecular reactant, substrate and tip identified.	Q4	On track
2 – Instrument development	System re-configured. Expected delivery and install in mid-May 2019.	Q2-6	On track
3 – Chemical synthesis	Revised synthetic path underway, with purity demonstrated at 4 of 16 steps.	Q4-5	On track
4 – Surface chemistry	Task contingent on completion of Task 3. Will be initiated in Q4.	Q4-6	On track
5 – Computational modeling	Trajectories for extraction of tip atom from Au tip simulated. Modeling of Au(111) surface in the presence of adamantane trithiol complete.	Q1-8	On track
6 – Tip chemistry	Task contingent on completion of Task 4. Will be initiated in Q6.	Q6-8	N/A

Transition Plan

New R&D platform

- Provide new toolsets and workflows for R&D applications in APM and potential commercial sales
- Further develop molecular toolsets to expand the library of applicable materials
- Explore partnership opportunities with manufacturers of commercial SPM systems to provide optimized, purpose-built instrumentation for APM applications

Intellectual Property

- Secure US competitiveness in a field of translatable R&D that is vibrant in Europe, Canada and Asia

Scaling for manufacturing applications

- Partner with commercial instrument manufacturers, potentially Scienta Omicron, to develop new instrumentation for higher throughput and flexibility to increase sales
    - Multiple probe SPM systems for APM
    - Non-SPM based platforms for mechanochemistry

UCLA

CNSI

From left: Prof. Yves Rubin. Sam Lilak. Prof. Philippe Sautet, Prof. James Gimzewski, Dr. Adam Stieg, Dr. Pallavi Bothra, Yolanda Li