

Palladium Thin Films for Hydrogen-Driven Actuation and Liquid Crystal Sensing in Microrobotics

2023 CNF REU Intern: Bryan Junsuh Kim

Intern Affiliation: Chemistry, University of California, Berkeley

CNF REU Principal Investigator: Nicholas Lawrence Abbott, Chemical & Biomolecular Engineering, Cornell
 CNF REU Mentor(s): Hanyu Alice Zhang, Ayushi Tripathi; Physics, Chemical & Biomolecular Engineering, Cornell
 Program & Primary Source of Research Funding: 2023 Cornell NanoScale Facility Research Experiences for Undergraduates (CNF REU) Program via the National Science Foundation under Grant No. NNCI-2025233
 Contact: bryanjskim@berkeley.edu, nla34@cornell.edu, hz496@cornell.edu, at885@cornell.edu
 Website(s): <https://cnf.cornell.edu/education/reu/2023>
 Primary CNF Tools Used: AJA3 Sputtering Deposition, ABM Contact Alignment, Zeiss SEM, Bruker Energy Dispersive X-ray Spectroscopy (EDS), Oxford PECVD, Critical Point Dryer

Abstract:

Microrobots rely on actuation and sensing as two key functions to navigate their environment. Chemomechanical actuation leverages gaseous fuels such as hydrogen to drive mechanical movement, while liquid crystals can sense hydrogen by generating an optical signal. Here, we study sputter-deposited thin films of palladium for micron-scale actuation and liquid crystal responsive sensors. Through a photolithographic process, we fabricate a palladium-titanium bimorph hinge between two silicon dioxide (SiO_2) panels, one fixed while the other free to rotate, as a working microactuator device. By exposing the microhinge to gaseous hydrogen, hydrogen diffuses into the palladium bulk and induces a phase transition from a hydrogen-poor α phase to a hydrogen-rich β phase in which the lattice parameter increases from 3.89 angstroms (\AA) to 4.03 \AA , bringing about a volumetric expansion that drives actuator bending. To promote faster actuation, we also introduce gold to create a palladium-gold alloy hinge, for the palladium-gold-hydride system facilitates a second-order phase transition with an alloy composition of 15-20% gold. Furthermore, our study reveals that sputter-deposited palladium induces surface anisotropy, observed via a preferential azimuthal direction of the liquid crystals when planarly aligned by hydrogen.

Summary of Research:

This research was conducted across two channels: fabricating microactuator devices and running hydrogen experiments for liquid crystal sensing.

Based on a past study in the Abbott group, the chemomechanical actuator device was composed of a platinum-titanium hinge between two SiO_2 panels: one fixed while the other free to rotate [1]. By applying gaseous hydrogen or oxygen, platinum surface stress drives reversible curvature changes for microactuation. A merit

of chemomechanical actuation is the circumvention of intermediate conversion processes (unlike photovoltaic actuators that convert light to voltage, then voltage to mechanical bending).

Here, platinum was switched out for palladium. Because gaseous species only interact with the platinum surface, the bending curvature is relatively weak. On the other hand, hydrogen diffuses into the palladium bulk and facilitates a phase transition from hydrogen-poor α -phase to hydrogen-rich β -phase. An increase in unit cell lattice parameter from 3.89 \AA to 4.03 \AA results in increased bulk volume [2]. Through bulk volumetric expansion instead of surface stress, a palladium-based actuator hinge can drive stronger mechanical bending than a platinum-based actuator hinge.

Through a photolithographic process, the palladium hinge actuators were fabricated. Two square SiO_2 panels, ten microns (μm) in length, were attached to a palladium-titanium hinge with dimensions 10 μm by 5 μm in length. The hinge was made by sputtering 50 nanometers (nm) of palladium on 10 nm of titanium. Additionally, a tether was attached to the bottom SiO_2 panel for support.

After fabrication, the devices were exposed to cycles of hydrogen and air. As observed in Figure 1, the actuation was gradual over three minutes of hydrogen exposure. Furthermore, the curvature change is jolty and abrupt rather than linear and smooth.

To remediate, gold was incorporated into the palladium hinge. In the palladium-hydride system, the transition from α to β is characterized by a 1st-order phase transition. Because the two phases must nucleate separately, an energy barrier exists. In the palladium-gold-hydride system, however, a 2nd-order phase transition is facilitated, meaning that phase separation is lost and the energy barrier is minimized. This absence of phase separation can lead to smoother, faster actuation.

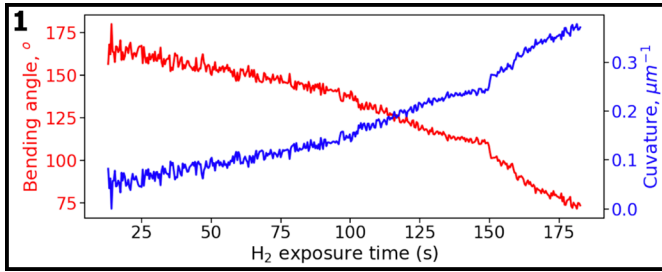


Figure 1: Hydrogen response for the Pd actuator hinge. Bending angle is defined as the angle between the two SiO₂ panels, and curvature is the change in the angle of deformation per unit length.

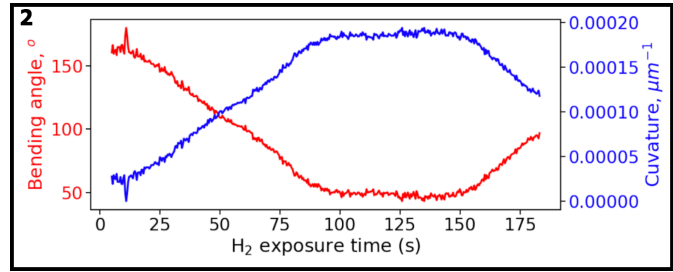


Figure 2: Hydrogen response for the palladium-gold actuator hinge.

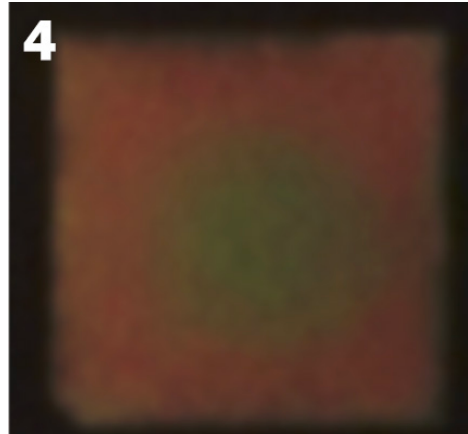
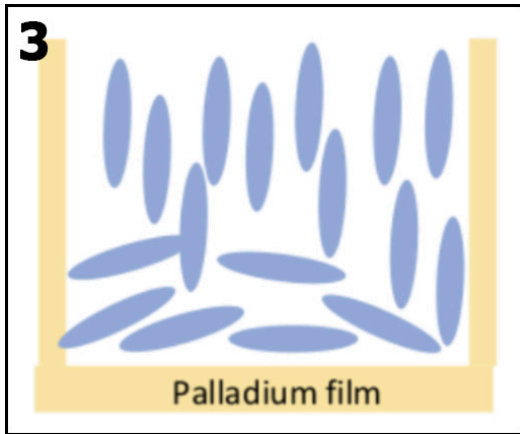


Figure 3, left: Side view of a schematic of planar-aligned 5CB liquid crystals on the surface of sputtered palladium thin film.
Figure 4, right: Top-down view of the bright optical response of 5CB liquid crystals on sputtered Pd.

From literature for the palladium-gold-hydride system, 15-20% gold concentration for a palladium-gold alloy is known to pass the critical point for phase separation [3].

The palladium-gold hinge was deposited via co-sputtering, which allowed tunable gold concentration. As shown in Figure 2, faster bending was observed over three minutes of hydrogen exposure. However, around 2.5 minutes, the hinge began to curve backwards, a behavior that remains to be investigated.

For liquid crystal sensing, 4-cyano-4'-pentylbiphenyl (5CB) liquid crystals were deposited on a sputtered palladium thin film. After two minutes of hydrogen exposure, the liquid crystals' surface alignment reoriented from homeotropic to planar as illustrated in Figure 3. The bright optical response is observed in Figure 4. Furthermore, it was discerned that the liquid crystals were uniformly aligned in a specific azimuthal direction. By rotating the sample along one of the cross-polarizer directions, the bright optical response briefly dimmed. Thus, sputtering deposition seems to induce surface anisotropy, observed by the preferential in-plane alignment of the liquid crystals.

Conclusions and Future Steps:

For the palladium-gold actuators, the hinge's behavior of curving backwards remains to be understood,

necessitating fabrication of more palladium-gold actuator samples. A possible explanation is crack formation in the hinge, causing hydrogen to drive out and reverting the α -to- β volumetric expansion.

For liquid crystal sensing, the origins of the surface anisotropy induced by sputtering remain to be investigated. Sputtering instrumentation parameters, such as target-to-substrate distances and angles, could elucidate so, as well as understanding the surface grain shape, orientation, etc.

Acknowledgements:

I would like to acknowledge the National Science Foundation (NSF) grant no. NNCI-2025233, the National Nanotechnology Coordinated Infrastructure (NNCI), and the Cornell NanoScale Facility for funding and curating the Research Experiences for Undergraduates (CNF REU) opportunity. I would also like to acknowledge and thank Prof. Nicholas Abbott, Alice Zhang, Ayushi Tripathi, and Tom Pennell for their research mentorship, as well as Melanie-Claire Mallison for her guidance as REU coordinator.

References:

- [1] Bao, N., et al. (2023). PNAS, 120(19).
- [2] Wang, B., et al. (2021). Micromachines, 12(11).
- [3] Maeland A., Flanagan, T.B. (1965). J. Phys. Chem., 1965, 69(10).